Conversion of Chiral Oxiranes into Chiral Aziridines with Retention of Configuration by Way of Chiral Episulfonium Ions and Reactions of the Aziridines with Grignard Reagents

Akio Toshimitsu,* Hideyuki Abe, Chitaru Hirosawa and Kohei Tamao
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Chiral oxiranes are converted into chiral aziridines with overall retention of configuration by means of sulfur chemistry. The key step of this procedure is the transformation of the organosulfur intermediates, *i.e.*, the replacement of a hydroxy group bound to a chiral carbon by a tosylamino group with retention of configuration through the anchimeric assistance of an arylsulfanyl group. The resulting tosylamines bearing the arylsulfanyl group on the β-carbon atom are cyclized to chiral aziridines through derivation to the sulfonium salt followed by intramolecular substitution of the sulfur moiety by the nitrogen atom. Ring opening of the chiral aziridines by Grignard reagents provides a useful procedure for the preparation of chiral amine derivatives.

Recently, various procedures have been reported for the preparation of chiral aziridines of both biological and chemical interest.[1] However, their preparations are still far from general as compared with those of chiral oxiranes.[2] We find a new procedure which converts chiral oxiranes into chiral aziridines with overall retention of configuration. This unprecedented stereospecificity is based on our recent findings that substitution reactions *via* chiral episulfonium ions (episulfonium ions bearing a chiral carbon in the ring) proceed with retention of configuration.[3] Thus, in the key step of this procedure, a hydroxy group bound to a chiral carbon is replaced by a tosylamino group with retention of configuration through the anchimeric assistance of an arylsulfanyl group. The resulting tosylamines bearing an arylsulfanyl group on the β-carbon atom are derivatized to the sulfonium salts, which are further treated with base to induce the intramolecular substitution of the sulfur moiety by the nitrogen atom to afford tosyl-protected chiral aziridines.[4] This procedure should be a good complement of the known procedure from oxiranes to aziridines with overall inversion of configuration.[1]

Reactions of aziridines with organometallic reagents[1,5,6] are comparatively unexplored as compared with those of oxiranes. There have been a few reports on the ring opening of aziridines by Grignard reagents.[1,5] Among these scattered reports, it has been shown that the regioselectivity of the ring opening of phenyl-substituted *N*-tosylaziridines by Grignard reagents depends on the amount of the Grignard reagent used,[5c] *i.e.*, whereas the reaction with one mole equivalent of Grignard reagent affords a mixture of regioisomers, the reaction with four mole equivalents affords the primary amine derivatives through selective attack on the benzylic carbon due to the interaction of the magnesium (of the excess of Grignard reagent) with the nitrogen atom. We have studied the reaction of aryl-substituted chiral aziridines with four mole equivalents of Grignard reagent and obtained two new findings as follows. (1) The regioselectivity of the ring opening depends on the nature of the carbon residue of the Grignard reagents, an allyl group attacking selectively on the benzylic carbon to afford the primary amine derivative. (2) This ring opening at the benzylic carbon proceeds without loss of optical purity, allowing the construction of chiral carbon through carbon–carbon bond formation. We have also studied the ring opening of alkyl-substituted aziridines by Grignard reagents and find that, in contrast to the results described above, all of the Grignard reagents examined attack selectively on the primary carbon, leaving the secondary (chiral) carbon intact.

We describe herein the details of these reactions as a new chiral pool method from easily accessible chiral oxiranes[2] to chiral amine derivatives with the incorporation of carbon nucleophiles.

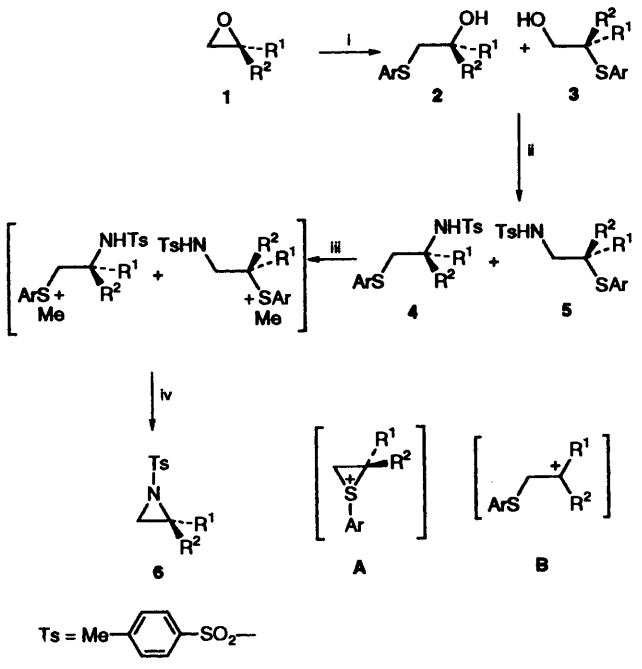
Results and Discussion

Preparation of Chiral Aziridines.—As shown in Scheme 1, our procedure consists of three steps. In the first step, chiral oxiranes **1** were transformed into chiral alcohols bearing an arylsulfanyl group on the β-carbon atom, regioisomers **2** and/or **3**. The second step is the key step of this procedure; *i.e.*, the hydroxy group bound to a chiral carbon was replaced by a tosylamino group with retention of configuration through the anchimeric assistance of the arylsulfanyl group *via* the chiral episulfonium ion **A**. The third step is the cyclization of the tosylamines bearing the arylsulfanyl group on the β-carbon atom, compounds **4** and/or **5**, to chiral aziridines **6**.

The first step was carried out by a reported reaction.[3a] As already reported, alkyl-substituted oxiranes afforded the alcohols **2** selectively, whereas aryl-substituted oxiranes afforded a mixture of regioisomers **2** and **3**.

The second step was carried out by reaction of the arylsulfanyl-substituted alcohol **2** or **3** with toluene-*p*-sulfonamide in dichloromethane in the presence of boron trifluoride–diethyl ether as catalyst. The yields and enantiomeric excesses (e.e.s) of the products, tosylamines bearing an arylsulfanyl group on the β-carbon atom, compounds **4** and/or **5**, are summarized in Table 1. In the case of the phenyl-substituted alcohol **2a** bearing a phenylsulfanyl group, this substitution reaction was accompanied by a partial racemization when carried out at −20 °C (entry 1). This racemization seems to proceed *via* the achiral open-chain carbenium ion **B** shown in Scheme 1, the formation of which is favoured by the presence of the phenyl group (R^1 = Ph).

At first, we tried to suppress the racemization by carrying out the reactions at lower temperatures. As shown in entries 2 and 3, the e.e.s of the tosylamine bearing a phenylsulfanyl group, **4a**, were improved, but with the sacrifice of the chemical yields even after prolonged reaction time. Then, we tried to suppress the racemization by stabilization of the chiral episulfonium ion **A** by the introduction of electron-donating substituent(s) into the phenyl group attached to the sulfur atom (compounds **2b–f**). By the introduction of one methyl group into the *para* position of the arylsulfanyl group (**2b**), the racemization was suppressed effectively to afford product **4b** in 99% e.e. with satisfactory



a; R^1 = Ar = Ph, R^2 = H
b; R^1 = Ph, R^2 = H, Ar = 4-MeC_6H_4
c; R^1 = Ph, R^2 = H, Ar = 4-$MeOC_6H_4$
d; R^1 = Ph, R^2 = H, Ar = 2,4-$Me_2C_6H_3$
e; R^1 = Ph, R^2 = H, Ar = 2,6-$Me_2C_6H_3$
f; R^1 = Ph, R^2 = H, Ar = 3,5-$Me_2C_6H_3$
g; R^1 = C_6F_5, R^2 = H, Ar = Ph
h; R^1 = n-C_6H_{13}, R^2 = H, Ar = Ph
i; R^1 = n-C_5H_{11}, R^2 = Me, Ar = 4-MeC_6H_4

Scheme 1 Transformation of chiral oxiranes to chiral aziridines. Structures **6a–f** are identical, and named **6b** in this paper owing to the preparation of compound **6b** from the secondary amine **4b** (see Table 2). *Reagents:* i, ArSNa; ii, $TsNH_2$, BF_3·Et_2O; iii, Me_3O^+ BF_4^-; iv, NaH.

chemical yield in the reaction at −20 °C (entry 5). It should be noted that the substitution reaction of compound **2b** was considerably accelerated compared with that for compound **2a**, and was complete within 2 h. The effect of the more electron-donating methoxy group was studied using *p*-methoxyphenyl derivative **2c** and the results are summarized in entries 6–8. The e.e.s of product **4c** were lower than those of the analogue **4b** produced in the reaction at the same temperature. The reaction time required for the consumption of the starting alcohol **2c** (TLC monitor) was also found to be longer than that for **2b**. These results show that the *p*-methoxyphenyl group is less effective than the *p*-tolyl group in the stabilization of the episulfonium ion **A** under the present conditions. We ascribed this unexpected result to the coordination of boron trifluoride to the oxygen atom of the *p*-methoxyphenyl group, which reduced the electron-donating ability of the group. Introduction of two methyl groups into the phenylsulfanyl group also provided unexpected effects, the reason being not clear yet. Thus, whereas 2,4- and 2,6-xylylsulfanyl-substituted alcohols **2d** and **2e** afforded the respective tosylamines **4d** and **4e** with unsatisfactory e.e.s (entries 9–11), 3,5-xylyl analogue **2f** did not afford compound **4f** even after all of the starting material was consumed (entry 12).

The participation of the *p*-tolylsulfanyl group was also utilized in the conversion of the chiral tertiary alcohol **2i** into the tosylamine **4i** to avoid racemization *via* the achiral tertiary carbenium ion (entry 15).

The hydroxy groups of the pentafluorophenyl-substituted secondary alcohol **2g** and aliphatic secondary alcohol **2h** were replaced by a tosylamino group without loss of optical purity through the participation of the phenylsulfanyl group (entries 13 and 14). The latter reaction, however, afforded a mixture of regioisomers **4h** and **5h**. This is a general tendency observed in other nucleophilic substitution reactions *via* episulfonium ion bearing one alkyl group.[3] It is emphasized here that all other reactions of the episulfonium ions bearing one aryl group or two alkyl groups with toluene-*p*-sulfonamide proceeded regioselectively at the more substituted carbon atom to afford products **4** (entries 1–13 and 15).

Starting from pentafluorophenyl-substituted primary alcohol **3g**, the regioisomer of secondary alcohol **2g**, the same chiral tosylamine **4g** was produced with the migration of the phenylsulfanyl group. This result suggests that the reactions of regioisomers **2g** and **3g** proceed through the same chiral episulfonium ion. The fission of the primary carbon–oxygen bond in compound **3g** seems to require more energy than does that of the secondary carbon–oxygen bond in compound **2g** to afford the common intermediate, as judged from the longer reaction time required for the completion of the reaction of primary alcohol **3g** (entry 18). When the phenyl-substituted primary alcohol **3b** was used as the substrate, the e.e. and the chemical yield of the tosylamine **4b** were quite unsatisfactory (entry 16). We acetylated the hydroxy group to improve its leaving ability and succeeded in transforming this substrate into compound **4b** in better e.e. and chemical yield (entry 17).

The third step of this procedure is the cyclization to the aziridines. Tosylamines bearing an arylsulfanyl group on the β-carbon atom, compounds **4** and/or **5**, were derivatized to the sulfonium salts, which were then treated with sodium hydride to induce an intramolecular substitution of the sulfur moiety by the nitrogen atom to afford the tosyl-protected chiral aziridines **6**. The results are summarized in Table 2. As shown in Table 2, the e.e.s of the aziridines were the same as those of the starting tosylamines within the range of experimental error. In the case of the aziridine bearing one alkyl group, compound **6h**, the enantiomers could not be separated by liquid chromatographic analyses using the chiral columns at hand: the e.e. in Table 2 refers to that of *N*-(2-methyldecan-4-yl)toluene-*p*-sulfonamide prepared from compound **6h** and isopropylmagnesium chloride through ring opening at the primary carbon, leaving the chiral carbon intact (*vide infra*).

The mixture of regioisomers (**4h** + **5h**) afforded compound **6h** quantitatively without loss of optical purity. This result indicates that both regioisomers afforded the same product with the same absolute configuration. This allows the formation of one chiral aziridine from one chiral oxirane irrespective of the presence of regioisomeric intermediates.

The use of the tosylamino group as a nitrogen source is important for this formation of aziridine, because acylamino groups have been reported to behave as oxygen nucleophiles to afford oxazoline derivatives in similar cyclizations.[7] To the best of our knowledge this procedure represents the first example of the N-alkylation of sulfonamides by sulfonium salts. In this connection, it should be noted here that the nitrogen atom of toluene-*p*-sulfonamide was alkylated twice during the overall transformation. In principle, this methodology would allow for the conversion of a wide range of substituted chiral oxiranes into chiral aziridines with overall retention of configuration.

Reaction of Chiral Aziridines with Grignard Reagents.—As an example of its utilization in organic syntheses, we investigated the ring opening of the aziridines by Grignard reagents such as alkyl-, aryl-, and allyl-magnesium halides. The results are summarized in Scheme 2 and Table 3.

Table 1 Yields and e.e.s of tosylamines bearing an arylsulfanyl group[a]

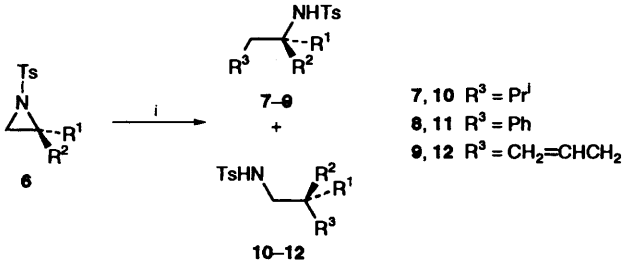
Entry	Alcohol	(% e.e.)	Temp.[b] (T/°C)	Time (t/h)	Product	Yield[c] (%)	e.e. (%)[d]
1	**2a**	(100)	−20	48	**4a**	73	77
2	**2a**	(100)	−35	48	**4a**	50	91
3	**2a**	(100)	−50	120	**4a**	27	99
4	**2b**	(100)	0	2	**4b**	72	87
5	**2b**	(100)	−20	2	**4b**	70	99
6	**2c**	(100)	0	5	**4c**	57	84
7	**2c**	(100)	−20	24	**4c**	78	96
8	**2c**	(100)	−40	67	**4c**	71	98
9	**2d**	(100)	0	5	**4d**	66	43
10	**2d**	(100)	−20	5	**4d**	81	85
11	**2e**	(100)	0	5	**4e**	87	2
12	**2f**	(100)	0	5			
13	**2g**	(96)	r.t.	2	**4g**	94	96
14	**2h**	(92)	r.t.	18	**4h**, **5h**	52, 33	91, 92
15	**2i**	(86)	−20	2	**4i**	66	84
16	**3b**	(100)	−20	24	**4b**	21	83
17	**3b** (Ac)[e]	(100)	−20	48	**4b**	47	92
18	**3g**	(97)	r.t.	96	**4g**	92	97

[a] Carried out using the alcohol (1 mmol), toluene-*p*-sulfonamide (2 mmol), and boron trifluoride–diethyl ether (5 mmol) in dichloromethane (5 cm^3). [b] r.t. = room temp. [c] Isolated yield by column chromatography. [d] Determined by liquid chromatography using chiral columns. [e] 2-[(4-Methylphenyl)sulfanyl]-2-phenylethyl acetate was used as the starting material.

Table 2 Yields and e.e.s of aziridines **6**[a]

Entry	Tosylamine	(% e.e.)	Aziridine	Yield (%)[b]	e.e. (%)[c]
1	**4b**	(99)	**6b**	91	98
2	**4g**	(96)	**6g**	93	95
3	**4h** + **5h**	(91)	**6h**	99	(90)[d]
4	**4i**	(83)	**6i**	81	83

[a] Carried out using 1.1 mol equiv. of $Me_3O^+BF_4^-$ and 1.5 mol equiv. of NaH. [b] Isolated yield by column chromatography. [c] Determined by liquid chromatographic analyses using chiral columns. [d] Determined after conversion into *N*-(2-methyldecan-4-yl)toluene-*p*-sulfonamide.



Scheme 2 Ring opening of aziridines by Grignard reagents. *Reagent:* i, R^3MgX.

In order to study the regioselectivity of the ring-opening reactions, we studied the reaction of racemic aziridines (±)-**6b**, -**6g**, -**6h** and -**6i** with four mole equivalents of a Grignard reagent. In the case of the aryl-substituted aziridines (±)-**6b** and -**6g**, the regioselectivity [the attack of Grignard reagent on the primary carbon to afford benzylic amine derivatives (±)-**7**–**9** *vs.* that on the benzylic carbon to afford primary amine derivatives (±)-**10**–**12**] was found to depend on the nature of the carbon residue of the Grignard reagent. The ratio of attack on the benzylic carbon increased in the following order of carbon residues: isopropyl < phenyl < allyl, allylmagnesium bromide attacking the benzylic carbon exclusively (Table 3, entries 1–3, 5 and 6). The observed regioselectivity may be ascribed to the ability of the interaction of the excess of Grignard reagent with the lone-pair electrons on the nitrogen atom of the aziridine as proposed by Kozikowski *et al.*,[5c] the interaction favouring the ring opening at the benzylic carbon. The order described above is in accord with the order of the polarizability of the carbon–magnesium bond of Grignard reagents. Thus, the interaction of the magnesium atom with the nitrogen atom would be more favoured in the reagents with the more polarized carbon–magnesium bond, such as the allyl–magnesium bond.

In the case of alkyl-substituted aziridines (±)-**6h** and -**6i**, on the other hand, all of the Grignard reagents examined attacked selectively on the primary carbon, to afford secondary amines (±)-**7h**–**9h** and (±)-**7i**–**9i** as the sole product (entries 7–12).

Conclusions.—This ring opening of chiral aziridines by Grignard reagents is shown to be useful in the preparation of chiral amine derivatives. The ring opening at the benzylic (chiral) carbon of compound **6b** by allylmagnesium bromide proceeded without loss of optical purity (Table 3, entry 3). Consideration of the reaction mechanism suggests that an inversion of configuration occurs during this ring opening, but we could not confirm the absolute configuration of product **12b**. Since the chiral carbon was kept intact during the ring opening at the primary carbon of substrates **6h** and **6i**, this reaction should also be valuable for the synthesis of chiral amine derivatives. In fact we confirmed that the e.e.s of the amines **7h** and **8i** are similar to those of the starting materials (tosylamines bearing an arylsulfanyl group, **4h** and **5h**, or the aziridine **6i**) (entries 7 and 11).

When combined with the stereoretentive conversion of chiral oxiranes into chiral aziridines, this ring-opening reaction should

Table 3 Products and yields of the reactions of aziridines with Grignard reagents[a]

Entry	Aziridine	Grignard reagent	Temp.[b] (T/°C)	Time (t/h)	Product (yield)[c]	Ratio[d]	e.e. (%)[e]
1	(±)-**6b**	Pr^iMgCl	0	6	**7b** + **10b** (63)	43:57	
2	(±)-**6b**	PhMgBr	r.t.	30	**8b** + **11b** (81)	9:91	
3	**6b**[f]	AllylMgBr	r.t.	24	**12b** (92)	0:100	94
4	(±)-**6g**	Pr^iMgCl	−20	48			
5	(±)-**6g**	PhMgBr	r.t.	22	**8g** + **11g** (100)	67:33	
6	(±)-**6g**	AllylMgBr	r.t.	3	**12g** (93)	0:100	
7	**6h**	Pr^iMgCl	r.t.	18	**7h** (85)	100:0	90
8	(±)-**6h**	PhMgBr	r.t.	18	**8h** (94)	100:0	
9	(±)-**6h**	AllylMgBr	r.t.	16	**9h** (76)	100:0	
10	(±)-**6i**	Pr^iMgCl	0	6	**7i** (81)	100:0	
11	**6i**	PhMgBr	r.t.	24	**8i** (81)	100:0	83
12	(±)-**6i**	AllylMgBr	r.t.	25	**9i** (100)	100:0	

[a] Carried out using the aziridine (0.5 mmol) and Grignard reagent (2.0 mmol) in THF (1.5 cm^3) under nitrogen. [b] r.t. = room temp. [c] Isolated yield by column chromatography. [d] Determined by integrals of the ^1H NMR spectrum. [e] Determined by liquid chromatographic analyses using chiral column. [f] **6b** of 94% e.e. was used.

allow the construction of chiral amines with various carbon frameworks by the proper choice of both the carbon moiety of the Grignard reagent and the substituents of the chiral oxirane.

Experimental

IR spectra were taken with a JASCO IR-810 spectrometer. ^1H NMR spectra were recorded with a Varian VXR-200 (200 MHz) instrument for solutions in $CDCl_3$ with $CHCl_3$ as internal standard (δ 7.25). J-Values are given in Hz. M.p.s were determined with a Shimadzu MM-2 or a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system, a Model 440 absorbance detector (at 254 nm), and a chiral column such as Daicel Chiralpak AD, AS or Chiralcel OD, OJ. Optical rotations were measured by a JASCO DIP-370 digital polarimeter for solutions in chloroform or ethanol. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}.

Materials.—Diethyl ether and tetrahydrofuran (THF) were dried over benzophenone ketyl and were distilled just before use. Dichloromethane was dried over calcium hydride and was distilled just before use. All other organic and inorganic materials were commercial products and were used without further purification.

The alcohols bearing an arylsulfanyl group on the β-carbon atom were prepared by the reported procedure.[3] Spectral and analytical data of compound **2a**, **3a**, **2g** and **3g** are already reported, and data of other alcohols are as follows.

(R)-2-[(4-*Methylphenyl*)*sulfanyl*]-1-*phenylethanol* **2b**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 49%; *liquid*; R_f 0.18 [hexane–ethyl acetate (5:1)] (Found: C, 73.55; H, 6.75. $C_{15}H_{16}OS$ requires C, 73.75; H, 6.6%); ν_{max}(liquid film)/cm^{-1} 3430, 3030, 2915 and 805; δ 2.34 (3 H, s), 2.90 (1 H, d, J 2.4), 3.03 (1 H, dd, J 14.0 and 9.6), 3.27 (1 H, dd, J 14.0 and 3.6), 4.67 (1 H, ddd, J 9.6, 3.6 and 2.4), 7.13 (2 H, d, J 7.8) and 7.23–7.43 (7 H, m); $[\alpha]_D^{19}$ +20 (c 0.276, $CHCl_3$) (100% e.e.). The optical purity of compound **2b** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (10:1) as eluent].

(S)-2-[(4-*Methylphenyl*)*sulfanyl*]-2-*phenylethanol* **3b**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (1:1) as eluent]; yield 48%; *liquid*; R_f 0.08 [hexane–ethyl acetate (5:1)] (Found: C, 73.4; H, 6.6%); ν_{max}(liquid film)/cm^{-1} 3400, 3030, 2910 and 810; δ 2.03 (1 H, t, J 6.6), 2.30 (3 H, s), 3.87 (1 H, dt, J 11.2 and 6.6), 3.91 (1 H, dt, J 11.2 and 6.6), 4.23 (1 H, t, J 6.6), 7.05 (2 H, d, J 8.2) and 7.15–7.38 (7 H, m); $[\alpha]_D^{21}$ +191 (c 0.356, $CHCl_3$) (100% e.e.). The optical purity of compound **3b** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (10:1) as eluent].

(R)-2-[(4-*Methoxyphenyl*)*sulfanyl*]-1-*phenylethanol* **2c**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 55%; *liquid*; R_f 0.21 [hexane–ethyl acetate (5:1)] (Found: C, 69.4; H, 6.4. $C_{15}H_{16}O_2S$ requires C, 69.2; H, 6.2%); ν_{max}(liquid film)/cm^{-1} 3440, 3030, 2930, 1240 and 815; δ 2.96 (1 H, d, J 2.2), 2.97 (1 H, dd, J 13.8 and 9.6), 3.19 (1 H, dd, J 13.8 and 3.4), 3.81 (3 H, s), 4.62 (1 H, ddd, J 9.6, 3.4 and 2.2), 6.82–6.93 (2 H, m), 7.23–7.28 (5 H, m) and 7.39–7.44 (2 H, m); $[\alpha]_D^{25}$ +18.2 (c 0.554, $CHCl_3$) (100% e.e.). The optical purity of compound **2c** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (6:1) as eluent].

(R)-2-[(2,4-*Dimethylphenyl*)*sulfanyl*]-1-*phenylethanol* **2d**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 53%; *liquid*; R_f 0.38 [hexane–ethyl acetate (5:1)] (Found: C, 74.45; H, 7.15. $C_{16}H_{18}OS$ requires C, 74.4; H, 7.0%); ν_{max}(liquid film)/cm^{-1} 3400, 3030, 2920 and 820; δ 2.30 (3 H, s), 2.41 (3 H, s), 2.88 (1 H, d, J 2.4), 2.91 (1 H, dd, J 13.6 and 9.6), 3.32 (1 H, dd, J 13.6 and 3.4), 4.67 (1 H, ddd, J 9.6, 3.4 and 2.4), 6.99 (1 H, d, J 8.2), 7.04 (1 H, s) and 7.24–7.40 (6 H, m); $[\alpha]_D^{25}$ −13.2 (c 0.539, $CHCl_3$) (100% e.e.). The optical purity of compound **2d** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (40:1) as eluent].

(R)-2-[(2,6-*Dimethylphenyl*)*sulfanyl*]-1-*phenylethanol* **2e**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (15:2) as eluent]; yield 49%; crystals; m.p. 66–67 °C; R_f 0.27 [hexane–ethyl acetate (5:1)] (Found: C, 74.45; H, 7.25%); ν_{max}(KBr)/cm^{-1} 3420, 3060, 2925, 775 and 700; δ 1.59 (1 H, br s), 2.57 (6 H, s), 2.84 (1 H, dd, J 13.3 and 9.4), 3.07 (1 H, dd, J 13.3 and 3.6), 4.59 (1 H, dd, J 9.4 and 3.6), 7.12 (3 H, s) and 7.24–7.39 (5 H, m); $[\alpha]_D^{25}$ −28.1 (c 0.538, $CHCl_3$) (100% e.e.). The optical purity of compound **2e** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (10:1) as eluent].

(R)-2-[(3,5-*Dimethylphenyl*)*sulfanyl*]-1-*phenylethanol* **2f**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 53%; *liquid*; R_f 0.33 [hexane–ethyl acetate (5:1)] (Found: C, 74.35; H, 7.15%); ν_{max}(liquid film)/cm^{-1} 3420, 3040, 2920, 850 and 700; δ 2.30 (6 H, s), 2.92 (1 H, d, J 2.4), 3.06 (1 H, dd, J 13.8 and 9.4), 3.31 (1 H, dd, J 13.8

and 3.6), 4.72 (1 H, ddd, *J* 9.4, 3.6 and 2.4), 6.87 (1 H, s), 7.04 (2 H, s) and 7.24–7.41 (5 H, m); $[\alpha]_D^{21}$ +7.2 (*c* 1.03, $CHCl_3$).

(R)-1-(*Phenylsulfanyl*)*octan*-2-*ol* **2h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 96%; *liquid*; R_f 0.20 [hexane–ethyl acetate (10:1)] (Found: C, 70.6; H, 9.45. $C_{14}H_{22}OS$ requires C, 70.55; H, 9.3%); ν_{max}(liquid film)/cm^{-1} 3400, 2940, 1590, 1490 and 740; δ 0.86 (3 H, t, *J* 6.8), 1.2–1.4 (8 H, m), 1.4–1.6 (2 H, m), 2.38 (1 H, br s), 2.83 (1 H, dd, *J* 13.6 and 8.8), 3.15 (1 H, dd, *J* 13.6 and 3.4), 3.50–3.73 (1 H, m) and 7.16–7.41 (5 H, m); $[\alpha]_D^{22}$ −32.6 (*c* 1.02, $CHCl_3$) (93% e.e.). The optical purity of compound **2h** was determined by ^1H NMR spectroscopy of its 'α-methoxy-α-trifluoromethyl-α-phenylacetate' (MTPA) ester.

(R)-2-*Methyl*-1-[(4-*methylphenyl*)*sulfanyl*]*heptan*-2-*ol* **2i**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (8:1) as eluent]; yield 90%; *liquid*; R_f 0.23 [hexane–ethyl acetate (8:1)] (Found: C, 71.05; H, 9.8. $C_{15}H_{24}OS$ requires C, 71.4; H, 9.6%); ν_{max}(liquid film)/cm^{-1} 3440, 3020, 2930 and 805; δ 0.86 (3 H, t, *J* 6.6), 1.13–1.41 (9 H, m), 1.45–1.63 (2 H, m), 2.16 (1 H, s), 2.30 (3 H, s), 3.04 (1 H, d, *J* 13.2), 3.08 (1 H, d, *J* 13.2), 7.08 (2 H, d, *J* 8.2) and 7.32 (2 H, d, *J* 8.2); $[\alpha]_D^{21}$ +29 (*c* 1.26, $CHCl_3$) (86% e.e.). The optical purity of compound **2i** was determined by HPLC analysis [Chiralpak AD; hexane–propan-2-ol (10:1) as eluent].

Reaction of (R)-2-[(4-*Methylphenyl*)*sulfanyl*]-1-*phenylethanol* **2b** *with Toluene*-p-*sulfonamide. General Procedure.*—To a mixture of the alcohol **2b** (245 mg, 1.00 mmol) and toluene-*p*-sulfonamide (205 mg, 1.20 mmol) was added dichloromethane (5.0 cm^3) under nitrogen. The resulting suspension was cooled to −20 °C and boron trifluoride–diethyl ether (0.61 cm^3, 5.0 mmol) was added to the mixture. After the precipitate of toluene-*p*-sulfonamide had disappeared (2 h), the reaction mixture was quenched by the addition of saturated aq. $NaHCO_3$ and the products were extracted with dichloromethane. The organic layer was dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography of the crude oily residue [silica gel; hexane–ethyl acetate (5:1) as eluent] afforded (R)-N-{2-[(4-*methylphenyl*)*sulfanyl*]-1-*phenylethyl*}*toluene*-p-*sulfonamide* **4b** (280 mg, 70%); crystals; m.p. 104–105 °C; R_f 0.16 [hexane–ethyl acetate (5:1)] (Found: C, 66.6; H, 6.0; N, 3.6. $C_{22}H_{23}NO_2S_2$ requires C, 66.45; H, 5.85; N, 3.5%); ν_{max}(KBr)/cm^{-1} 3240, 3010, 2920, 1320, 1160 and 800; δ 2.33 (3 H, s), 2.37 (3 H, s), 3.13 (1 H, dd, *J* 13.8 and 6.6), 3.17 (1 H, dd, *J* 13.8 and 7.4), 4.24 (1 H, dt, *J* 4.2 and 6.8), 5.29 (1 H, d, *J* 4.2), 6.98–7.28 (11 H, m) and 7.49 (2 H, d, *J* 8.4); $[\alpha]_D^{19}$ +1 (*c* 0.276, $CHCl_3$) (99% e.e.). The optical purity of compound **4b** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (7:1) as eluent].

Spectral and analytical data of other tosylamines bearing an arylsulfanyl group on the β-carbon atoms are as follows.

(R)-N-[1-*Phenyl*-2-(*phenylsulfanyl*)*ethyl*]*toluene*-p-*sulfonamide* **4a**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (2:1) as eluent]; yield 27%; *crystals*; m.p. 101–102 °C; R_f 0.14 [hexane–ethyl acetate (5:1)] (Found: C, 65.4; H, 5.6; N, 3.4. $C_{21}H_{21}NO_2S_2$ requires C, 65.75; H, 5.5; N, 3.65%); ν_{max}(KBr)/cm^{-1} 3270, 3060, 2920, 1330, 1155, 805 and 665; δ 2.36 (3 H, s), 3.18 (1 H, dd, *J* 14.0 and 6.8), 3.21 (1 H, dd, *J* 14.0 and 7.2), 4.28 (1 H, dt, *J* 4.8 and 6.9), 5.41 (1 H, d, *J* 4.8), 7.01–7.38 (12 H, m) and 7.47–7.55 (2 H, m); $[\alpha]_D^{19}$ −8.2 (*c* 0.593, $CHCl_3$) (99% e.e.). The optical purity of compound **4a** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (7:1) as eluent].

(R)-N-{2-[(4-*Methoxyphenyl*)*sulfanyl*]-1-*phenylethyl*}*toluene*-p-*sulfonamide* **4c**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (4:1) as eluent]; yield 71%; *liquid*; R_f 0.18 [hexane–ethyl acetate (4:1)] (Found: C, 63.9; H, 5.55; N, 3.2. $C_{22}H_{23}NO_3S_2$ requires C, 63.9; H, 5.6; N, 3.4%); ν_{max}(liquid film)/cm^{-1} 3270, 3040, 2940, 1330, 1250, 1160, 805 and 665; δ 2.73 (3 H, s), 3.06 (2 H, d, *J* 7.0), 3.81 (3 H, s), 4.21 (1 H, dt, *J* 4.4 and 7.0), 5.36 (1 H, d, *J* 4.4), 6.79 (2 H, d, *J* 8.4), 7.00–7.22 (9 H, m) and 7.49 (2 H, d, *J* 8.2); $[\alpha]_D^{24}$ +2.9 (*c* 1.01, $CHCl_3$) (98% e.e.). The optical purity of compound **4c** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (4:1) as eluent].

(R)-N-{2-[(2,4-*Dimethylphenyl*)*sulfanyl*]-1-*phenylethyl*}*toluene*-p-*sulfonamide* **4d**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 81%; *liquid*; R_f 0.11 [hexane–ethyl acetate (10:1)] (Found: C, 67.15; H, 6.15; N, 3.3. $C_{23}H_{25}NO_2S_2$ requires C, 67.1; H, 6,1; N, 3.4%); ν_{max}(liquid film)/cm^{-1} 3275, 3020, 2910, 810 and 660; δ 2.27 (3 H, s), 2.30 (3 H, s), 2.35 (3 H, s), 3.09 (2 H, d, *J* 7.0), 4.26 (1 H, dt, *J* 4.4 and 7.0), 5.19 (1 H, d, *J* 4.4), 6.86–7.24 (10 H, m) and 7.47 (2 H, d, *J* 8.2); $[\alpha]_D^{21}$ −1.8 (*c* 1.30, $CHCl_3$) (85% e.e.). The optical purity of compound **4d** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (40:1) as eluent].

(R)-N-{2-[(2,6-*Dimethylphenyl*)*sulfanyl*]-1-*phenylethyl*}-*toluene*-p-*sulfonamide* **4e**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 87%; crystals; m.p. 128–130 °C; R_f 0.11 [hexane–ethyl acetate (10:1)] (Found: C, 67.1; H, 6.35; N, 3.4%); ν_{max}(KBr)/cm^{-1} 3260, 3040, 2940, 1320, 1155, 780, 700 and 670; δ 2.36 (3 H, s), 2.41 (6 H, s), 2.95 (1 H, dd, *J* 13.2 and 6.6), 3.03 (1 H, dd, *J* 13.2 and 7.0), 4.28 (1 H, dt, *J* 5.4 and 6.5), 5.09 (1 H, d, *J* 5.4), 6.97–7.25 (10 H, m) and 7.44 (2 H, d, *J* 8.4). The optical purity of compound **4e** was determined by HPLC analysis [Chiralcel OD, hexane–propan-2-ol (10:1) as eluent].

(R)-N-[1-(*Pentafluorophenyl*)-2-(*phenylsulfanyl*)*ethyl*]*toluene*-p-*sulfonamide* **4g**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 94%; *crystals*; m.p. 117–118 °C; R_f 0.18 [hexane–ethyl acetate (5:1)] (Found: C, 53.15; H, 3.35; N, 2.95. $C_{21}H_{16}F_5NO_2S_2$ requires C, 53.25; H, 3.4; N, 2.95%); ν_{max}(KBr)/cm^{-1} 3280, 3060, 2940, 1340, 1160 and 810; δ 2.36 (3 H, s), 3.22 (1 H, dd, *J* 14.0 and 8.8), 3.33 (1 H, dd, *J* 14.0 and 6.6), 4.79 (1 H, dt, *J* 6.6 and 8.8), 5.68 (1 H, d, *J* 8.8), 7.10–7.29 (7 H, m) and 7.57 (2 H, d, *J* 8.4); $[\alpha]_D^{21}$ +17 (*c* 2.30, $CHCl_3$) (96% e.e.). The optical purity of compound **4g** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (5:1) as eluent].

(R)-N-{1-[(*Phenylsulfanyl*)*octan*-2-*yl*]*toluene*-p-*sulfonamide*} **4h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 52%; *crystals*; m.p. 75–77 °C; R_f 0.13 [hexane–ethyl acetate (10:1)] (Found: C, 64.3; H, 7.45; N, 3.75. $C_{21}H_{29}NO_2S_2$ requires C, 64.4; H, 7.45; N, 3.6%); ν_{max}(KBr)/cm^{-1} 3300, 3080, 2925, 2850, 1340, 1150 and 670; δ 0.82 (3 H, t, *J* 6.7), 0.91–1.67 (10 H, m), 2.38 (3 H, s), 2.79 (1 H, dd, *J* 13.4 and 6.8), 3.13 (1 H, dd, *J* 13.4 and 4.3), 3.23–3.43 (1 H, m), 4.64 (1 H, d, *J* 8.0), 7.13–7.38 (7 H, m) and 7.63 (2 H, d, *J* 8.4); $[\alpha]_D^{23}$ −32 (*c* 0.319, $CHCl_3$) (91% e.e.). The optical purity of compound **4h** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (20:1) as eluent].

(S)-N-[2-(*Phenylsulfanyl*)*octyl*]*toluene*-p-*sulfonamide* **5h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 33%; *liquid*; R_f 0.29 [hexane–ethyl acetate (5:1)] (Found: C, 64.5; H, 7.45; N, 3.45%); ν_{max}(liquid film)/cm^{-1} 3280, 3060, 2930, 1325, 1160, 810 and 665; δ 0.86 (3 H, t, *J* 6.6), 1.15–1.61 (10 H, m), 2.43 (3 H, s), 2.8–3.1 (3 H, m),

4.96 (1 H, t, *J* 6.2), 7.15–7.34 (7 H, m) and 7.68 (2 H, d, *J* 8.2); $[\alpha]_D^{24}$ +152 (*c* 0.391, $CHCl_3$) (91% e.e.). The optical purity of compound **5h** was determined by HPLC analysis [Chiralcel OD; hexane–propan-2-ol (30:1) as eluent].

(R)-N-[2-*Methyl*-1-{[(4-*methylphenyl*)*sulfanyl*]*heptan*-2-*yl*}*toluene*-p-*sulfonamide* **4i**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 66%; *crystals*; m.p. 67–69 °C; R_f 0.29 [hexane–ethyl acetate (5:1)] (Found: C, 65.3; H, 7.85; N, 3.3. $C_{22}H_{31}NO_2S_2$ requires C, 65.15; H, 7.7; N, 3.45%); ν_{max}(KBr)/cm^{-1} 3270, 3030, 2940, 1315, 1160, 810 and 665; δ 0.80 (3 H, t, *J* 6.7), 0.94–1.35 (6 H, m), 1.20 (3 H, s), 1.40–1.64 (2 H, m), 2.30 (3 H, s), 2.38 (3 H, s), 2.99 (1 H, d, *J* 13.2), 3.10 (1 H, d, *J* 13.2), 5.05 (1 H, s), 7.07 (2 H, d, *J* 8.0), 7.22 (4 H, d, *J* 8.0) and 7.74 (2 H, d, *J* 8.4); $[\alpha]_D^{21}$ +187 (*c* 0.67, $CHCl_3$) (81% e.e.). The optical purity of compound **4i** was determined by HPLC analysis [Chiralpak AD; hexane–propan-2-ol (6:1) as eluent].

Preparation of (R)-2-(*Pentafluorophenyl*)-1-*tosylaziridine* **6g**. *General Procedure*.—To a mixture of the tosylamine bearing a phenylsulfanyl group **4g** (1.42 g, 3.00 mmol) and trimethyloxonium tetrafluoroboranuide (488 mg, 3.30 mmol) was added dichloromethane (15 cm^3) under nitrogen. After being stirred for 5 h at ambient temperature, the mixture was evaporated under reduced pressure. Sodium hydride (the oily dispersion was washed with hexane and dried *in vacuo*; 108 mg, 4.50 mmol) was added to the residual solid and the air was replaced by nitrogen. THF (15 cm^3) was added into the mixture and the resulting suspension was stirred for 18 h at ambient temperature. The reaction was quenched by the addition of water and the products were extracted with dichloromethane. The organic layer was dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography of the crude oil [silica gel; hexane–ethyl acetate (10:1) as eluent] afforded (R)-2-(*pentafluorophenyl*)-1-*tosylaziridine* **6g** (1.02 g, 93%); crystals; m.p. 99–100 °C; R_f 0.23 [hexane–ethyl acetate (5:1)] (Found: C, 49.5; H, 2.75; N, 3.85. $C_{15}H_{10}F_5NO_2S$ requires C, 49.6; H, 2.75; N, 3.85%); ν_{max}(KBr)/cm^{-1} 3015, 2940, 1330, 1165 and 825; δ 2.46 (3 H, s), 2.79 (1 H, d, *J* 4.4), 3.03 (1 H, d, *J* 7.2), 3.79 (1 H, dd, *J* 7.2 and 4.4), 7.36 (2 H, d, *J* 8.4) and 7.85 (2 H, d, *J* 8.4); $[\alpha]_D^{21}$ −56 (*c* 4.00, $CHCl_3$) (95% e.e.). The optical purity of compound **6g** was determined by HPLC analysis [Chiralpak AS; hexane–propan-2-ol (10:1) as eluent].

Spectral and analytical data of other aziridines are as follows.

(R)-2-*Phenyl*-1-*tosylaziridine* **6b**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 91%; crystals; m.p. 86–87 °C (lit.,[5b] 90–91 °C); $[\alpha]_D^{21}$ −102 (*c* 1.80, $CHCl_3$) (98% e.e.). The optical purity of compound **6b** was determined by HPLC analysis [Chiralpak AS; hexane–propan-2-ol (2:1) as eluent].

(R)-2-*Hexyl*-1-*tosylaziridine* **6h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 99%; *liquid*; R_f 0.26 [hexane–ethyl acetate (10:1)] (Found: C, 63.8; H, 8.45; N, 4.8. $C_{15}H_{23}NO_2S$ requires C, 64.0; H, 8.25; N, 5.0%); ν_{max}(liquid film)/cm^{-1} 2940, 1320, 1160, 810 and 660; δ 0.84 (3 H, t, *J* 6.5), 1.07–1.65 (10 H, m), 2.05 (1 H, d, *J* 4.4), 2.44 (3 H, s), 2.63 (1 H, d, *J* 7.0), 2.63–2.77 (1 H, m), 7.33 (2 H, d, *J* 8.2) and 7.82 (2 H, d, *J* 8.2); $[\alpha]_D^{21}$ +2 (*c* 0.37, $CHCl_3$).

(R)-2-*Methyl*-2-*pentyl*-1-*tosylaziridine* **6i**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 81%; *liquid*; R_f 0.29 [hexane–ethyl acetate (10:1)] (Found: C, 63.75; H, 8.5; N, 4.8%); ν_{max}(liquid film)/cm^{-1} 3040, 2940, 1320, 1160 and 830; δ 0.87 (3 H, t, *J* 6.5), 1.16–1.67 (8 H, m), 1.61 (3 H, s), 2.27 (1 H, s), 2.42 (3 H, s), 2.54 (1 H, s), 7.30 (2 H, d, *J* 8.4) and 7.82 (2 H, d, *J* 8.4); $[\alpha]_D^{21}$ −17 (*c* 1.06, $CHCl_3$) (83% e.e.). The optical purity of compound **6i** was determined by HPLC analysis [Chiralpak AS; hexane–propan-2-ol (10:1) as eluent].

Reaction of (R)-2-*Methyl*-2-*pentyl*-1-*tosylaziridine* **6i** *with Phenylmagnesium Bromide. General Procedure*.—To a solution of the aziridine **6i** (116 mg, 0.41 mmol; 83% e.e.) in THF (2.0 cm^3) was added phenylmagnesium bromide (3.0 mol dm^{-3} solution in Et_2O; 0.53 cm^3, 1.59 mmol) under nitrogen. After being stirred for 24 h at ambient temperature, the reaction mixture was quenched by the addition of water and the products were extracted with dichloromethane. The organic layer was dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography of the crude oil [silica gel; hexane–ethyl acetate (10:1) as eluent] afforded (R)-N-[2-*methyl*-1-*phenylheptan*-2-*yl*]*toluene*-p-*sulfonamide* **8i** (120 mg, 81%); crystals; m.p. 77–80 °C; R_f 0.09 [hexane–ethyl acetate (10:1)] (Found: C, 69.85; H, 8.1; N, 3.9. $C_{21}H_{29}NO_2S$ requires C, 70.15; H, 8.15; N, 3.9%); ν_{max}(KBr)/cm^{-1} 3280, 3030, 2950, 1320 and 1150; δ 0.84 (3 H, t, *J* 6.5), 1.0–1.3 (6 H, m), 1.10 (3 H, s), 1.3–1.5 (2 H, m), 2.40 (3 H, s), 2.83 (1 H, d, *J* 13.2), 2.91 (1 H, d, *J* 13.2), 4.49 (1 H, s), 7.17–7.34 (7 H, m) and 7.71 (2 H, d, *J* 8.0); $[\alpha]_D^{21}$ −2 (*c* 2.80, $CHCl_3$) (83% e.e.). The optical purity of compound **8i** was determined by HPLC analysis [Chiralpak AS; hexane–propan-2-ol (10:1) as eluent].

Spectral and analytical data of other tosylamines are as follows.

Mixture of N-[3-*Methyl*-1-*phenylbutyl*]*toluene*-p-*sulfonamide* **7b** *and* N-[3-*Methyl*-2-*phenylbutyl*]*toluene*-p-*sulfonamide* **10b**.—Although pure substrate **7b** or **10b** was not isolated, column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent] afforded fractions enriched with compounds **7b** and **10b** respectively, which allowed the assignment of ^1H NMR signals; total yield (**7b** + **10b**) 63%; liquid; R_f 0.29 [hexane–ethyl acetate (5:1)] (Found: M^+, 317.1438. $C_{18}H_{23}NO_2S$ requires *M*, 317.1449); ν_{max}(liquid film)/cm^{-1} 3300, 2960, 1328, 1157, 705 and 670; δ (**7b**) 0.80 (3 H, d, *J* 6.4), 0.84 (3 H, d, *J* 7.2), 1.4–1.7 (3 H, m), 2.33 (3 H, s), 4.32 (1 H, q, *J* 7.4), 5.08 (1 H, d, *J* 7.4), 6.9–7.4 (7 H, m) and 7.49 (2 H, d, *J* 8.2); (**10b**) 0.64 (3 H, d, *J* 6.8), 0.92 (3 H, d, *J* 6.6), 1.6–1.9 (1 H, m), 2.2–2.5 (1 H, m), 2.44 (3 H, s), 3.00 (1 H, ddd, *J* 12.2, 10.6 and 3.2), 3.46 (1 H, ddd, *J* 12.2, 9.0 and 4.6), 4.00–4.17 (1 H, m), 6.9–7.4 (7 H, m) and 7.62 (2 H, d, *J* 8.2).

(R)-N-(2-*Methyldecan*-4-*yl*)*toluene*-p-*sulfonamide* **7h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 85%; *liquid*; R_f 0.23 [hexane–ethyl acetate (10:1)] (Found: C, 66.25; H, 9.75; N, 4.2. $C_{18}H_{31}NO_2S$ requires C, 66.4; H, 9.6; N, 4.3%); ν_{max}(liquid film)/cm^{-1} 3280, 3040, 2940, 1330, 1160 and 810; δ 0.72 (3 H, d, *J* 6.6), 0.84 (3 H, t, *J* 6.4), 0.89 (3 H, d, *J* 6.6), 1.0–1.4 (12 H, m), 1.4–1.7 (1 H, m), 2.41 (3 H, s), 3.13–3.34 (1 H, m), 4.14 (1 H, d, *J* 8.6), 7.28 (2 H, d, *J* 8.2) and 7.74 (2 H, d, *J* 8.2); $[\alpha]_D^{21}$ −7 (*c* 2.50, $CHCl_3$). The optical purity of compound **7h** was determined by HPLC analysis [Chiralpak AS; hexane–propan-2-ol (10:1) as eluent].

N-(2,4-*Dimethylnonan*-4-*yl*)*toluene*-p-*sulfonamide* **7i**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 81%; liquid; R_f 0.17 [hexane–ethyl acetate (10:1)] (Found: C, 66.6; H, 9.45; N, 4.25%); ν_{max}(liquid film)/cm^{-1} 3280, 2950, 2870, 1320, 1150, 810 and 665; δ 0.83 (3 H, t, *J* 6.8), 0.89 (3 H, d, *J* 6.6), 0.92 (3 H, d, *J* 6.8), 1.02–1.78 (11 H, m), 1.13 (3 H, s), 2.41 (3 H, s), 4.35 (1 H, s), 7.26 (2 H, d, *J* 8.2) and 7.75 (2 H, d, *J* 8.2).

Mixture of N-(1,2-*Diphenylethyl*)*toluene*-p-*sulfonamide* **8b** *and* N-(2,2-*Diphenylethyl*)*toluene*-p-*sulfonamide* **11b**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield (**8b** + **11b**) 81%; *solid*; R_f 0.11 [hexane–ethyl acetate (5:1)] (Found: C, 71.95; H, 6.1; N, 3.85. $C_{21}H_{21}NO_2S$ requires C, 71.75; H, 6.0; N, 4.0%); ν_{max}(KBr)/cm^{-1} 3300, 1330, 1162, 705 and 665; δ (**8b**) 2.35 (3 H, s), 2.98 (2 H, d, *J* 6.6), 4.50 (1 H, q, *J* 6.6), 4.96 (1 H, d, *J* 6.6), 7.0–7.4 (12 H, m) and 7.41 (2 H, d, *J* 8.4); (**11b**) 2.44 (3 H, s), 3.55 (2 H, dd, *J* 8.0 and 6.2), 4.06 (1 H, t, *J* 8.0), 4.41 (1 H, t, *J* 6.2), 7.04–7.32 (12 H, m) and 7.68 (2 H, d, *J* 8.2).

Mixture of N-[1-(*Pentafluorophenyl*)-2-*phenylethyl*]*toluene*-p-*sulfonamide* **8g** *and* N-[2-(*Pentafluorophenyl*)-2-*phenylethyl*]-*toluene*-p-*sulfonamide* **11g**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield (**8g** + **11g**) 100%; *solid*; R_f 0.18 (hexane–ethyl acetate (5:1)] (Found: M$^+$, 441.0806. $C_{21}H_{16}F_5NO_2S$ requires *M*, 441.0821); ν_{max}(KBr)/cm^{-1} 3270, 1521, 1503, 1329, 1158, 973 and 700; δ (**8g**) 2.35 (3 H, s), 2.98 (1 H, dd, *J* 13.6 and 8.2), 3.18 (1 H, dd, *J* 13.6 and 7.0), 4.87–4.99 (1 H, m), 5.09 (1 H, d, *J* 9.0), 6.93–6.98 (2 H, m), 7.1–7.3 (3 H, m), 7.11 (2 H, d, *J* 8.2) and 7.49 (2 H, d, *J* 8.2); (**11g**) 2.43 (3 H, s), 3.73 (2 H, t, *J* 7.5), 4.53 (1 H, t, *J* 8.2), 4.67 (1 H, br s), 7.0–7.5 (7 H, m) and 7.66 (2 H, d, *J* 8.4).

N-(1-*Phenyloctan*-2-*yl*)*toluene*-p-*sulfonamide* **8h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 94%; *liquid*; R_f 0.13 [hexane–ethyl acetate (10:1)] (Found: C, 70.1; H, 8.35; N, 3.85. $C_{21}H_{29}NO_2S$ requires C, 70.15; H, 8.15; N, 3.9%); ν_{max}(liquid film)/cm^{-1} 3280, 3040, 2930, 1325, 1160, 810 and 665; δ 0.82 (3 H, t, *J* 6.2), 0.97–1.60 (10 H, m), 2.40 (3 H, s), 2.68 (2 H, d, *J* 6.2), 3.32–3.50 (1 H, m), 4.23 (1 H, d, *J* 8.0), 6.98–7.07 (2 H, m), 7.16–7.32 (5 H, m) and 7.65 (2 H, d, *J* 8.2).

N-(*Undec*-1-*en*-5-*yl*)*toluene*-p-*sulfonamide* **9h**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (10:1) as eluent]; yield 76%; *liquid*; R_f 0.14 [hexane–ethyl acetate (10:1)] (Found: C, 66.75; H, 9.05; N, 4.2. $C_{18}H_{29}NO_2S$ requires C, 66.85; H, 8.95; N, 4.35%); ν_{max}(liquid film)/cm^{-1} 3180, 3080, 2930, 1640, 1330, 1160, 810 and 670; δ 0.83 (3 H, t, *J* 6.8), 0.95–1.60 (12 H, m), 1.89–2.05 (2 H, m), 2.41 (3 H, s), 3.13–3.29 (1 H, m), 4.24 (1 H, d, *J* 8.4), 4.84–4.98 (2 H, m), 5.68 (1 H, ddt, *J* 16.5, 9.7 and 6.6), 7.28 (2 H, d, *J* 8.2) and 7.74 (2 H, d, *J* 8.2).

N-(5-*Methyldec*-1-*en*-5-*yl*)*toluene*-p-*sulfonamide* **9i**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 100%; *liquid*; R_f 0.11 [hexane–ethyl acetate (5:1)] (Found: M$^+$, 323.1901. $C_{18}H_{29}NO_2S$ requires *M*, 323.1918); ν_{max}(liquid film)/cm^{-1} 3260, 2940, 1641, 1323, 1155, 810 and 670; δ 0.84 (3 H, t, *J* 6.6), 1.05–1.32 (6 H, m), 1.13 (3 H, s), 1.37–1.59 (4 H, m), 1.88–2.03 (2 H, m), 2.41 (3 H, s), 4.35 (1 H, s), 4.86–5.03 (2 H, m), 5.75 (1 H, ddt, *J* 16.6, 10.2 and 6.4), 7.26 (2 H, d, *J* 8.2) and 7.75 (2 H, d, *J* 8.2).

(S)-N-[2-*Phenylpent*-4-*enyl*]*toluene*-p-*sulfonamide* **12b**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 92%; crystals; m.p. 62–63 °C (lit.,[5b] 62–64 °C); $[\alpha]_D^{21}$ −1 (*c* 1.90, $CHCl_3$) (94% e.e.). The optical purity of compound **12b** was determined by HPLC analysis [Chiralpak AD; hexane–propan-2-ol (10:1) as eluent].

N-[2-(*Pentafluorophenyl*)*pent*-4-*enyl*]*toluene*-p-*sulfonamide* **12g**.—Isolated by column chromatography [silica gel; hexane–ethyl acetate (5:1) as eluent]; yield 93%; *solid*; R_f 0.14 [hexane–ethyl acetate (5:1)] (Found: C, 53.05; H, 4.0; N, 3.45. $C_{18}H_{16}F_5NO_2S$ requires C, 53.35; H, 4.0; N, 3.45%); ν_{max}(KBr)/cm^{-1} 3250, 3060, 2920, 965 and 920; δ 2.23–2.56 (2 H, m), 2.42 (3 H, s), 3.18–3.40 (3 H, m), 4.72 (1 H, s), 4.88–5.08 (2 H, m), 5.53 (1 H, ddt, *J* 15.8, 11.2 and 7.4), 7.57 (2 H, d, *J* 8.2) and 7.62 (2 H, d, *J* 8.2).

Acknowledgements

We are grateful to Professor Shigeo Tanimoto of our Institute for helpful discussions during the early stages of this work. We also thank the Japan Energy Co. Ltd. for donating (*R*)-hexyloxirane, (*R*)-2-methyl-2-pentyloxirane, (*R*)-phenyloxirane and (*R*)-(pentafluorophenyl)oxirane.

References

1 For an excellent review, see D. Tanner, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 599.
2 R. A. Johnson and K. B. Sharpless, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1987, vol. 7, p. 389; K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu and X.-L. Zhang, *J. Org. Chem.*, 1992, **57**, 2768; B. B. Lohray, *Tetrahedron Asymmetry*, 1992, **3**, 1317; R. A. Johnson and K. B. Sharpless, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, p. 447; K. Furuhashi, *J. Synth. Org. Chem. Jpn.*, 1987, **45**, 162; G. Solladié, G. Demailly and C. Greck, *Tetrahedron Lett.*, 1985, **26**, 435.
3 A. Toshimitsu, C. Hirosawa and S. Tanimoto, (*a*) *Tetrahedron Lett.*, 1991, **32**, 4317; (*b*) *Chem. Lett.*, 1992, 239.
4 Preliminary communication: A. Toshimitsu, H. Abe, C. Hirosawa and S. Tanimoto, *J. Chem. Soc., Chem. Commun.*, 1992, 284.
5 The ring opening of activated aziridines by Grignard reagents: (*a*) H. M. I. Osborn and J. B. Sweeney, *Tetrahedron Lett.*, 1994, **35**, 2739; (*b*) L. S. Hegedus and J. M. McKearin, *J. Am. Chem. Soc.*, 1982, **104**, 2444; (*c*) A. P. Kozikowski, H. Ishida and I. Isobe, *J. Org. Chem.*, 1979, **44**, 2788; (*d*) W. Oppolzer and E. Flaskamp, *Helv. Chim. Acta*, 1977, **60**, 204.
6 Recent reports on the ring opening of aziridines by organometallic reagents: T. Ibuka, K. Nakai, H. Habashita, N. Fujii, F. Garrido, A. Mann, Y. Chounan and Y. Yamamoto, *Tetrahedron Lett.*, 1993, **34**, 7421; H. Ohno, A. Mori and S. Inoue, *Chem. Lett.*, 1993, 975; H. M. I. Osborn, J. B. Sweeney and B. Howson, *Synlett.*, 1993, 675.
7 B. M. Trost and T. Shibata, *J. Am. Chem. Soc.*, 1982, **104**, 3225.

Paper 4/03673E
Received 17*th June* 1994
Accepted 6*th August* 1994