Desymmetrization of *N*-Sulfonated Aziridines by Alkyllithium Reagents in the Presence of Chiral Ligands

by **Paul Müller***, **David Riegert**, and **Gérald Bernardinelli**

Department of Organic Chemistry, University of Geneva, 30, Quai Ernest Ansermet, CH-1211 Geneva 4
(phone: +41 22 379 65 27; fax: +41 22 379 32 15; e-mail: paul.muller@chiorg.unige.ch)

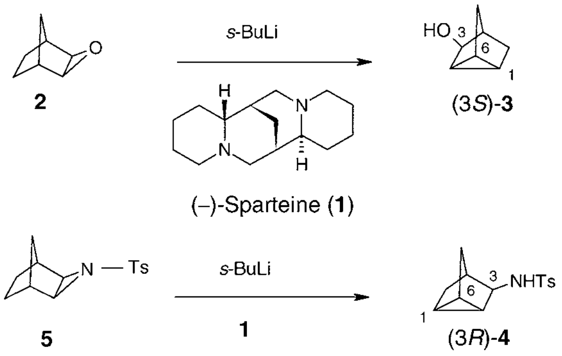
The stereochemical course of the rearrangement of the *N*-sulfonylaziridines **5**, **15**, and **25** in the presence of *s*-BuLi/(−)-sparteine to the bicyclic sulfonamides **4**, **16**, and **17**, respectively, has been investigated chemically and by X-ray structure analysis. The absolute configurations of the products were, in all cases, opposite to those of the alcohols formed upon rearrangement of the corresponding epoxides. Similarily, the allylic sulfonamide **10**, resulting from rearrangement of 7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane (**7**) under the same reaction conditions, had the (*R*)-configuration, while cyclohexen-3-ol, obtained upon rearrangement of cyclohexene oxide, is known to be (*S*)-configured. Deuterium labelling showed that the rearrangement of **7** proceeds *via* enantioselective α-elimination to a carbene, which undergoes a 1,2-H shift.

Introduction. – Epoxides containing β-H-atoms react with lithium-amide bases *via* β-elimination to afford alcohols [1]. The application of this reaction to the desymmetrization of *meso*-epoxides has been extensively investigated [2]. However, deprotonation may also occur at the α-position to afford α-lithiated epoxides, which may react further to form a variety of products [3]. In the presence of a strong organolithium base, the α-lithiated epoxide is formed irreversibly and, in the absence of stabilizing groups, may undergo α-elimination. The resulting α-lithiooxycarbene yields products typical for carbenoid reactions, such as CH-bond insertion, 1,2-H shifts, and cyclopropanations [4]. When the α-deprotonation of a *meso*-epoxide is carried out in the presence of a chiral ligand such as sparteine [5], the reaction products may be enantiomerically enriched [6].

N-Sulfonylaziridines, which may be considered nitrogen analogs of epoxides, react only sluggishly and unselectively with lithium amide bases [7]. However, they do yield products derived from apparent carbenoid pathways, when exposed to organolithium bases. We have recently reported the desymmetrization of *N*-sulfonated aziridines derived from simple cyclic olefins by *s*-BuLi in the presence of (−)-sparteine (**1**; *Scheme 1*) [8]. The reaction proceeds in analogy to that of the corresponding epoxides and affords enantiomerically enriched allylic or bicyclic sulfonamides. The absolute configuration of one of the rearrangement products was determined by chemical correlation. Surprisingly, while reaction of *exo*-norbornene oxide (**2**) with *s*-BuLi in the presence of (−)-sparteine afforded nortricyclanol (**3**) mainly with the (3*S*)-configuration, the major enantiomer of the sulfonamide **4**, resulting from the analogous reaction of the corresponding aziridine **5**, had the (3*R*)-configuration.

The stereochemical course of the aziridine rearrangement has not yet been established beyond doubt. The sulfonamide **4** showed a very low optical rotation

Scheme 1



($[\alpha]_D = -0.7$ for 43% ee) and, although the value was consistent with that of an independently prepared sample, we had some doubts. Accordingly, we looked for an independent determination of the configuration of **4** to confirm the discrepancy between the stereochemical course of rearrangement of **2** and **5**. In the affirmative situation, it was of interest to establish whether the stereochemical discrepancy was general or limited to the above case. At the same time, we investigated the rearrangement of some other aziridines in order to examine the scope of the reaction.

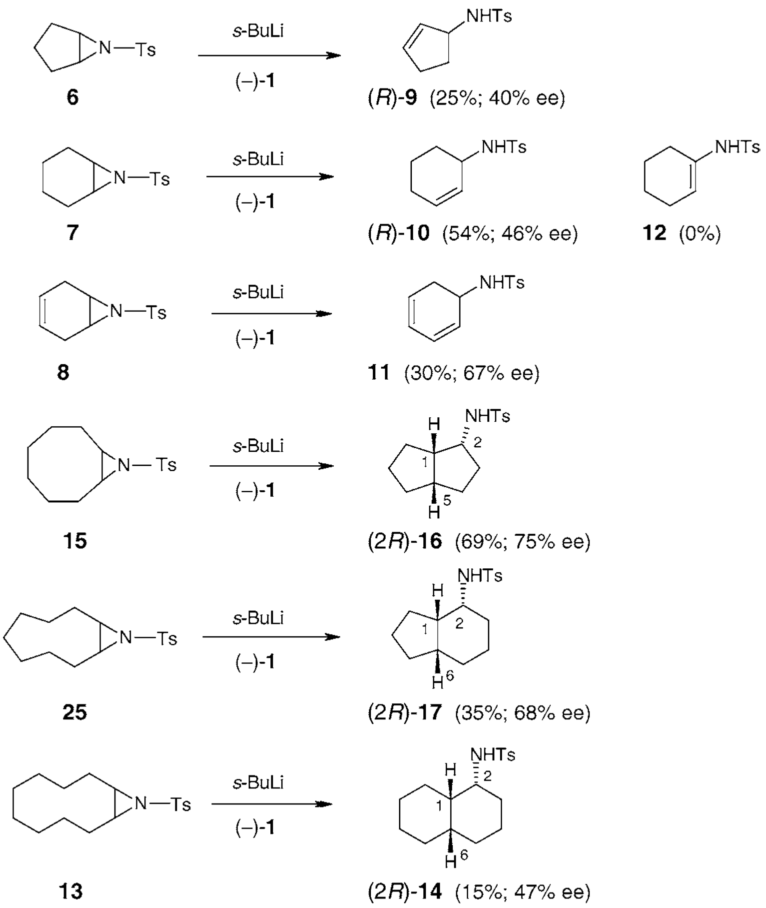
2. Results and Discussion. – 2.1. *Variation of Aziridines and Chiral Ligands. N*-Tosylated aziridines were synthesized *via* reaction of the appropriate olefins with TsN=IPh[1]) in the presence of [Cu(OTf)$_2$] as catalyst (see *Exper. Part*). The rearrangement was carried out with *s*-BuLi (3.0 equiv.) and (−)-sparteine (**1**; 3.0 equiv.) in Et$_2$O at −78° (5 h), followed by warming to room temperature overnight. The aziridines **6**, **7**, and **8** afforded the allylic sulfonamides **9**, **10**, and **11** (*Scheme 2* and *Table 1*). In the case of **7**, the previously reported enamide **12** was not observed, but the yield of **10** increased from 35 to 54%. Exclusive formation of allylic sulfonamides upon reaction of **7** with *s*-BuLi/(−)-sparteine [9] or (i-Pr)$_2$NLi/*t*-BuOK [10] has been observed by other investigators. The aziridines derived from medium-sized rings, in turn, reacted under the same conditions to afford bicyclic sulfonamides in analogy to the norbornene derivative **5**. We were intrigued to find substantial variations in yield according to the structure of the starting aziridines in the formation of both allylic as well as bicyclic sulfonamides, and some experiments were carried out to shed some light on this phenomenon (*Table 1*). First, we note that with *s*-BuLi alone (in the absence of ligand), the yield of **10** dropped to 7%, but the product was accompanied by a substantial amount of TsNH$_2$ (70%) (*Entry 2*). The origin of TsNH$_2$ was not further investigated, but **10** was stable upon exposure to *s*-BuLi/**1**, which rules out an eventual subsequent β-elimination of **10**. In the presence of *s*-BuLi/TMEDA[2]) (2.8 equiv), the yield of **10** was equally low (14%), and TsNH$_2$ was formed in 68% yield. The highest

---

[1]) '[*N*-(*p*-toluenesulfonyl)imino]phenyliodane' (=4-methyl-*N*-((*E*)-phenyl-λ^3-iodanylidene]benzenesulfonamide.

[2]) TMEDA = 'Tetramethyl ethylenediamine' (Me$_2$N(CH$_2$)$_2$NMe$_2$).

Scheme 2

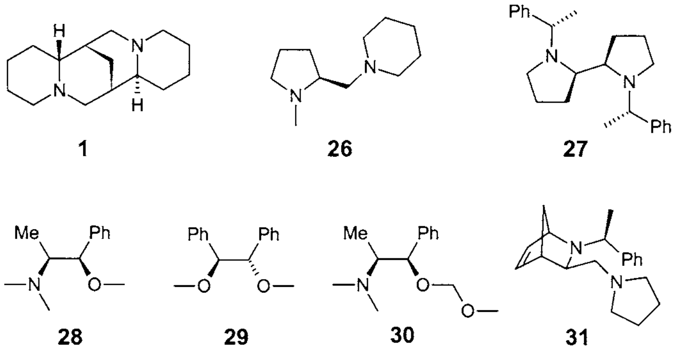


yield (54%) resulted upon reaction with *s*-BuLi/sparteine. Similarily, the reaction of **13** with *s*-BuLi/(–)-sparteine, where the yield of the insertion product **14** is low (15%; *Entry 5*), was accompanied by 73% of $TsNH_2$. When ether was replaced by THF as solvent, the yield of **10** decreased to 21%, with 22% ee (*Entry 4*).

The structure of the organic moiety remaining after formation of $TsNH_2$ was not determined owing to its volatility. Therefore, we have no information on the course of the elimination. There seems to be competition between the reactions leading to carbene-derived products *vs.* $TsNH_2$. Apparently, coordination of the organilithium reagent to sparteine favors the carbenoid pathway.

Several chiral ligands were examined with **15** as substrate in the hope of improving both the yield and enantioselectivity of the reaction (*Table 1*). Sparteine was, in this respect, clearly the most-effective ligand. Among the other ligands tested, we found that tertiary diamines were more efficient than amino ethers or diethers. However, no general conclusions can be drawn from this limited series of ligands.

Table 1. *Effect of Ligands on the Yield and Enantioselectivity of Aziridine Rearrangements*a). Ts = 4-$MeC_6H_4SO_2$; ee = enantiomeric excess.



Entry	Aziridine	Ligand	Product	Yield [%]	ee [%]	$TsNH_2$ [%]
1	**7**	**1**	**10**	54	46 (*R*)	b)
2	**7**	none	**10**	7	–	70
3	**7**	TMEDA2)	**10**	14	–	68
4	**7**	**1**c)	**10**	21	22	b)
5	**13**	**1**	**14**	15	47 (2*R*)	73
6	**15**	**1**	**16**	69	75 (2*R*)	b)
7	**15**	**26**	**16**	66	24 (2*R*)	b)
8	**15**	**27**	**16**	60	11 (2*R*)	b)
9	**15**	**31**	**16**	37	9 (2*R*)	b)
10	**15**	**28**	**16**	14	4	b)
11	**15**	**29**	**16**	13	19 (2*S*)	b)
12	**15**	**30**	**16**	7	3	b)

a) Conditions: see *Exper. Part* (*Sect. 3*). b) Not determined. c) In THF.

2.2. *Absolute Configurations.* The minor enantiomer of **4** was separated by semi-preparative HPLC, and X-ray crystal-structure analysis confirmed the (3*S*)-configuration (*Fig. 1,a*). Thus, the major enantiomer of the rearrangement of **5** in the presence of (–)-sparteine had the (3*R*)-configuration. The previous assignment was, therefore, confirmed. Recrystallization of the bicyclic sulfonamides **16** and **17** provided enantiomerically pure samples investigated by X-ray analysis (*Figs. 1,b* and *1,c*, resp.). HPLC Studies showed that the crystals corresponded indeed to the major enantiomers. Compounds **16** and **17** are *cis*-configured at the ring junction, the sulfonamido group being *endo*. In both cases, the absolute configuration at C(2) is (*R*)3). The (2*R*)-configuration of **16** has been independently confirmed by chemical correlation [9].

The absolute configuration of **10** can be derived from its optical rotation: the experimental value is $[\alpha]_D^{21} = +19.8$ ($c = 1.50$, $CHCl_3$) for 39% ee. Comparison with the known value for (*S*)-**10** ($[\alpha]_D^{24} = -51.1$ ($c = 1.51$, $CHCl_3$) [11] for 67% ee leads to the assignment of the (*R*)-configuration for **10**. The configurations of the other products were not determined. However, a tentative assignment was made for (*R*)-**9** on the

---

3) Atom numbering according to *Scheme 2*, not *Fig. 1* (arbitrary numbering of X-ray structures).

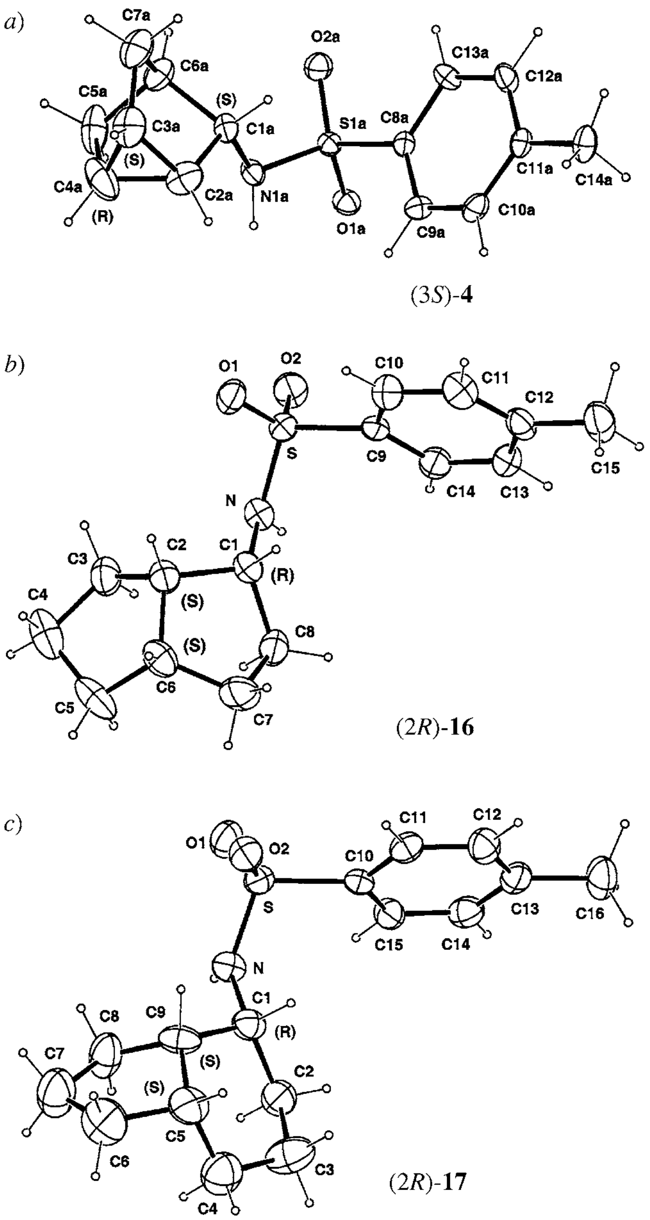


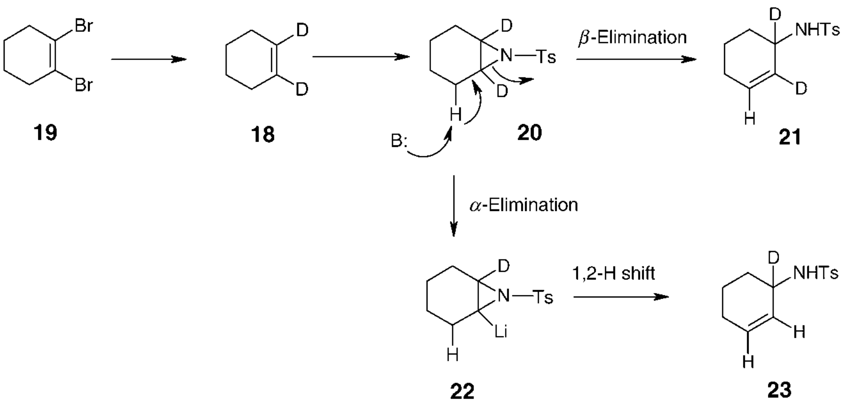
Fig. 1. *X-Ray crystal structures of compounds (3*S*)-**4**, (2*R*)-**16**, and (2*R*)-**17***[3]). See also *Table 2* and the X-ray section in the *Exper. Part.*

grounds of its optical rotation ($[\alpha]_D^{25} = +11.4$). The optical rotations of several derivatives of (*R*)-cyclopent-2-en-1-amines are positive (*N*-Boc derivative: $[\alpha]_D^{23} = +77.0$ [12]; benzamide: $[\alpha]_D^{23} = +76.3$ [12]; *N*-methylbenzamide: $[\alpha]_D^{21} = +49.7$) [12]), which indicates the (*R*)-configuration for **9**, whose derivatives are all dextrorotatory

[13]. This tentative assignment has been experimentally confirmed by others [9]. Similarily, the sign of the optical rotation of the sulfonamides **16**, **17**, and **14** is positive, while that of the corresponding (2*S*)-configured bicyclic alcohols is negative (*endo-cis*-bicyclo[3.3.0]octan-2-ol: $[\alpha]_D^{25} = -104$ [14]; *endo-cis*-bicyclo[4.3.0]nonan-2-ol: $[\alpha]_D^{21} = -27.2$ [6a]; *endo-cis*-bicyclo[4.4.0]decan-2-ol: $[\alpha]_D^{21} = -22$ [15]). Since the (*R*)-configuration of **16** and **17** was established, and since there was no change in the sign of the optical rotations of **16**, **17**, and **14**, the configuration of **14** should be (2*R*).

Thus, in all cases where the configuration of the sulfonamide had been established, it was opposite to that of the correponding alcohols resulting from the analogous epoxide rearrangement with *s*-BuLi/(−)-sparteine. This unexpected stereochemical outcome could be of mechanistic origin. In the case of the epoxide rearrangement with *s*-BuLi/sparteine, a mechanism involving α-deprotonation followed by carbene insertion into a transannular C−H bond to yield bicyclic products, or by 1,2-H migration to afford allylic alcohols, is well accepted [2a], although allylic alcohols may also occur upon β-elimination [2d,e]. We have proposed an α-elimination mechanism for the aziridine rearrangement for reasons of analogy to the epoxide rearrangement [8]. To further investigate this issue, we studied the rearrangement of **7** by means of deuterium labelling: 1,2-dideuteriocyclohexene (**18**), synthesized by reduction of 1,2-dibromocyclohexene (**19**) [16][17], was aziridinated to **20** with TsN=IPh in the presence of [Cu(acac)$_2$] (*Scheme 3*). Rearrangement of **20** *via* β-elimination would afford the allylic sulfonamide **21**, having only one olefinic H-atom. α-Deprotonation, in turn, would yield the lithiated aziridine, which would undergo α-elimination to the lithiated carbene **22**, followed by 1,2-H migration to afford the sulfonamide **23**, with two olefinic H-atoms present. In *Fig. 2*, the relevant part of the ^{1}H-NMR spectrum of undeuterated **10** is shown, together with that of the reaction product **23**. The spectrum exhibits clearly two resonances for olefinic H-atoms. In addition, the expected signal for H−C(3) at 3.79 ppm is absent in the ^{1}H-NMR spectrum of **23**. This result is, thus, consistent with a mechanism involving α-elimination of **20**. The mechanisms of the other reactions were not investigated, but are assumed to involve α-elimination as well for reasons of analogy to the rearrangement of the corresponding epoxides. Please note,

Scheme 3



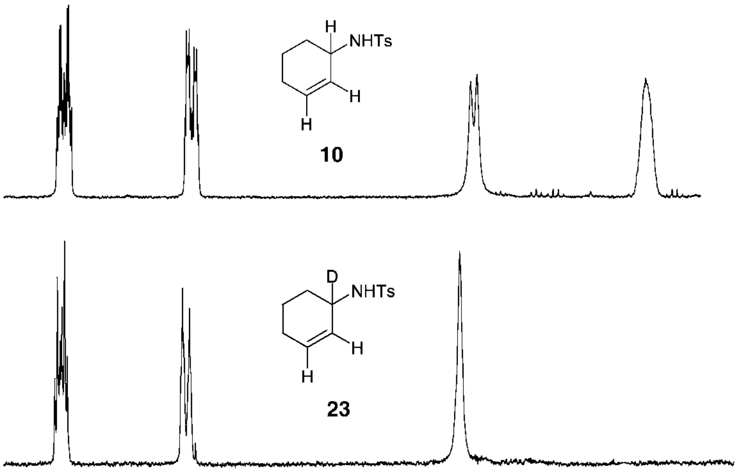
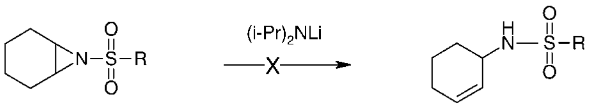


Fig. 2. *Selected signals of the* ^{1}*H-NMR spectra of compounds* **10** (top) *and* **23** (bottom)

however, that our results do not exclude a transannular elimination mechanism [18] for the formation of the bicyclic tosylamides.

Contrary to epoxides, *N*-sulfonated or *N*-phosphinoylated aziridines are unreactive towards lithium amide bases [7]. An attempt was made to increase the reactivity of the aziridines by replacement of the *p*-toluenesulfonyl (Ts) group by 4-nitrophenylsulfonyl (Ns), 2,4-dinitrophenylsulfonyl, or trifluoromethylsulfonyl groups (*Scheme 4*). However, exposure of **7a** or **7b** to LDA did not lead to any reaction, and **7c** decomposed under the reaction conditions to a complex mixture of products.

Scheme 4

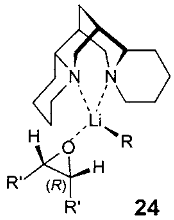


7a–c

a R = 4-(NO$_2$)C$_6$H$_5$
b R = 2,4-(NO$_2$)$_2$C$_6$H$_4$
c R = F$_3$C

10a–c

The enantioselectivity of the epoxide desymmetrization with *s*-BuLi/sparteine has been rationalized with a model based on coordination of the *s*-BuLi/sparteine complex to the epoxide O-atom. Upon complexation, the enantiotopic H-atoms of the epoxide become diastereotopic, and selective deprotonation at the (*R*)-configured stereocenter occurs within the coordination complex **24** [2a]. This model may not apply to *N*-sulfonylaziridines, where the steric situation is quite different because of the presence of the bulky sulfo group. This steric difference may provoke a change in the enantioselectivity of metallation. In addition, the lone pair of the N-atom is delocalized and looses part of its basic character so that association with *s*-BuLi/sparteine will be disfavored. This is particularly the case in coordinating solvents such as Et$_2$O. However, complexation of the aziridine with the *s*-BuLi/sparteine complex is not a requirement for enantioselective metallation, since this complex is chiral by itself. However, in view of the complexity of the association phenomena of lithium-amide bases [19], and in view of our limited knowledge of the system, it is too early to advance a model for the enantioselective metallation of *N*-sulfonyl aziridines.



24

3. Conclusions. – The desymmetrization of *N*-sulfonylaziridines with *s*-BuLi/sparteine gives rise to allylic or bicyclic sulfonamides, respectively, according to ring size. The reaction may also be effected with other chiral ligands, such as tertiary diamines, amino ethers, or diethers, although sparteine is far superior. In all cases investigated so far, the stereochemical outcome of the aziridine desymmetrization is opposite to that of the correponding epoxides. The origin of this difference is not yet fully understood.

This work was supported by the *Swiss National Science Foundation* (Projects No. 20-52581.97 and 2027-048156), and by the *European Commission for Science, Research and Development* (COST Action D12). The authors are indebted to *A. Pinto* and *J.-P. Saulnier* for the NMR spectra and to *D. Klink* for the mass spectra. We wish to express our gratitude to *T. Katsuki* and *P. O'Brien* for communication of unpublished data, and to *P. O'Brien* for clarifiying discussions.

Experimental Part

1. *General.* See [20]. FC = flash chromatography.

2. *Synthesis of Aziridines.* The aziridines were synthesized by Cu-catalyzed aziridination of the appropriate olefins with TsN=IPh [21], 4-$NO_2C_6H_4N$=IPh [22], or 2,4-$(NO_2)_2C_6H_3SO_2N$=IPh [20], respectively. For data of **5** and **7**, see [23]; for **6**, see [24]; for **7a** see [25]; for **8**, see [26]; for **15**, see [27].

7-[(2,4-Dinitrophenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane (**7b**). Yield 31%. M.p. 158°. IR ($CHCl_3$): 3020*w*, 2946*w*, 1556*m*, 1541*m*, 1348*m*, 1226*m*, 1168*w*, 794*m*, 666*s*. ^1H-NMR (500 MHz, $CDCl_3$): 1.28–1.31 (*m*, 2 H); 1.39–1.41 (*m*, 2 H); 1.90–1.96 (*m*, 4 H); 3.37 (*m*, 2 H); 8.45 (*d*, J = 8.6, 1 H); 8.57 (*d*, J = 8.6, 1 H); 8.60 (*s*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.2 (*t*); 22 .8 (*t*); 43.6 (*d*); 119.9 (*d*); 126.5 (*d*); 132.6 (*d*); 138.4 (*s*); 150.0 (*s*). Anal. calc. for $C_{12}H_{13}N_3O_6S$: C 44.03, H 4.00, N 12.84; found C 44.06, H 3.93, N 12.77.

7-[(Trifluoromethyl)sulfonyl]-7-azabicyclo[4.1.0]heptane (**7c**). To 7-azabicyclo[4.1.0]heptane [11] (172 mg, 1.8 mmol) and Et_3N (0.4 ml, 1.8 mmol) in Et_2O (5.0 ml) was added trifluoroacetic acid (TFA) anhydride (0.38 ml, 1.8 mmol) at 10°. The temp. of the mixture was allowed to reach r.t. within 12 h. The mixture was then hydrolyzed with sat. aq. NH_4Cl soln. (10 ml). The aq. layer was extracted with Et_2O (3 × 10 ml), and the combined org. layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by FC (AcOEt/pentane 1:9) to afford **7c** (142 mg, 46%). Yellow oil. IR ($CHCl_3$): 2947*s*, 2867*m*, 1793*s*, 1460*m*, 1364*s*, 1227*s*, 1131*s*, 970*s*, 919*s*, 848*s*, 650*s*. ^1H-NMR (500 MHz, $CDCl_3$): 1.32–1.34 (*m*, 2 H); 1.47–1.50 (*m*, 1 H); 1.92–2.01 (*m*, 4 H); 3.29–3.32 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.9 (*t*); 22.6 (*t*); 42.8 (*d*); 115.2 (*q*, $J_{C,F}$ = 318). ^{19}F-NMR (470 MHz, $CDCl_3$, rel. to C_6F_6): 86.4 (*s*). MS: 229 (< 1, M^+), 205 (16), 190 (100), 162 (55), 136 (37), 98 (11), 96 (51), 81 (17), 78 (10), 69 (53), 67 (11), 57 (27), 56 (21), 55 (15), 54 (17). HR MS: 229.0368 (M^+, $C_7H_{10}F_3NO_2S^+$; calc. 229.0384).

10-[(4-Methylphenyl)sulfonyl]-10-azabicyclo[7.1.0]decane (**25**). From cyclononene [28], in 52% yield. M.p. 60–62°. IR ($CHCl_3$): 3685*w*, 2928*m*, 2855*w*, 1600*w*, 1318*w*, 1157*m*, 774*s*, 746*s*, 720*s*, 672*s*. ^1H-NMR (500 MHz, $CDCl_3$): 1.32–1.66 (*m*, 12 H); 1.93–1.98 (*m*, 2 H); 2.45 (*s*, 3 H); 2.76–2.80 (*m*, 2 H); 7.32 (*d*, J = 7.8, 2 H); 7.81

(*d*, *J* = 7.8, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.6 (*q*); 22.9 (*t*); 23.0 (*t*); 23.6 (*t*); 23.9 (*t*); 45.7 (*d*); 127.6 (*d*); 129.6 (*d*); 135.8 (*s*); 144.1 (*s*). MS: 294 (<1, M^+), 139 (11), 138 (100), 91 (33), 69 (53), 55 (28). HR-MS: 294.1522 (M^+, $C_{16}H_{24}NO_2S^+$; calc. 294.1528).

11-[(4-Methylphenyl)sulfonyl]-11-azabicyclo[8.1.0]undecane (**13**). From *cis*-cyclodecene (*Fluka*), in 41% yield. M.p. 112 – 115°. IR ($CHCl_3$): 3019*w*, 2929*w*, 1474*w*, 1319*m*, 1228*w*, 1156*s*, 1091*m*, 977*w*, 837*m*, 794*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.33 – 1.77 (*m*, 16 H); 2.43 (*s*, 3 H); 2.79 (*m*, 2 H); 7.29 (*s*, *J* = 8, 2 H); 7.81 (*d*, *J* = 8, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.5 (*q*); 22.9 (*t*); 23.0 (*t*); 23.6 (*t*); 23.7 (*t*); 23.9 (*t*); 45.8 (*d*); 127.5 (*d*); 129,7 (*d*); 135.8 (*s*); 144.0 (*s*). MS: 307 (<1, M^+), 153 (11), 152 (100), 91, 69 (16), 55 (19). HR MS: 307.1592 (M^+, $C_{17}H_{25}NO_2S^+$; calc. 307.1606).

3. *Desymmetrization of Aziridines. General Procedure:* To *s*-BuLi (0.74 ml, 1.3M soln. in hexane, 0.96 mmol) in Et_2O (2.0 ml) was added at – 78° (–)-sparteine (225 mg, 0.96 mmol) in Et_2O (1.0 ml). After 1 h at – 78°, the aziridine (0.32 mmol) was added, and stirring was continued for 4 h at – 78°. The temp. was allowed to reach r.t. overnight. The mixture was hydrolyzed with sat. aq. NH_4Cl soln. (10 ml). The aq. phase was extracted with Et_2O (3 × 10 ml), the combined org. layers were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by FC.

For data of **4**, **10**, and **16**, see [8].

Rearrangement of **6** *to* (R)-N-*(cyclopent-2-en-1-yl)-4-methylbenzenesulfonamide* [29] (**9**). FC (SiO_2; AcOEt/pentane 1:9): 25%. Colorless solid. M.p. 64 – 66°. $[\alpha]_D^{25} = +11.4$ ($c = 0.5$, $CHCl_3$) for 40% ee. IR ($CHCl_3$): 3020*m*, 2330*w*, 1515*w*, 1214*s*, 1157*w*, 743*s*, 668*m*, 455*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.93 – 2.18 (*m*, 2 H); 2.21 – 2.38 (*m*, 2 H); 2.43 (*s*, 3 H); 3.50 – 3.59 (*m*, 1 H); 4.35 (br., 1 H); 5.30 – 5.71 (*m*, 2 H); 7.35 (*d*, *J* = 7.8, 2 H); 7.73 (*d*, *J* = 7.8, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.5 (*q*); 29.6 (*t*); 31.5 (*t*); 59.8 (*d*); 127.0 (*d*); 129.6 (*d*); 130.4 (*d*); 135.1 (*d*); 138.1 (*s*); 143.3 (*s*). MS: 237 (3, M^+), 173 (11), 92 (12), 91 (53), 83 (13), 82 (100), 71 (10), 67 (31), 66 (14), 65 (23), 57 (20), 55 (62). HR MS: 237.0820 (M^+, $C_{12}H_{15}NO_2S^+$; calc. 237.0823).

Rearrangement of **8** *to* N-*(cyclohexa-2,4-dien-1-yl)-4-methylbenzenesulfonamide* (**11**). FC (SiO_2; AcOEt/pentane 2:8): 30%. Colorless crystals. M.p. 63 – 65°. $[\alpha]_D^{20} = +101$ ($c = 2.07$, $CHCl_3$) for 67% ee. IR ($CHCl_3$): 3022*m*, 2359*w*, 1226*w*, 1159*w*, 796*m*, 744*m*, 666*s*, 483*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.34 – 2.41 (*m*, 2 H); 2.42 (*s*, 3 H); 3.86 – 4.00 (*m*, 1 H); 4.60 – 4.64 (br., 1 H); 5.50 – 5.59 (*m*, 1 H); 5.71 – 5.80 (*m*, 1 H); 5.92 – 5.99 (*m*, 2 H); 7.27 – 7.31 (*d*, *J* = 8, 2 H); 7.72 – 7.76 (*d*, *J* = 8, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.6 (*q*); 30.4 (*t*); 46.2 (*d*); 123.8 (*d*); 124.9 (*d*); 126.5 (*d*); 127.3 (*d*); 128.3 (*d*); 129.7 (*d*). MS: 249 (3, M^+), 171 (46), 155 (11), 149 (12), 107 (14), 106 (49), 95 (12), 94 (100), 93 (50), 92 (22), 91 (71), 79 (23), 78 (29), 71 (13), 69 (12), 67 (88), 66 (25), 65 (45), 57 (243), 55 (16), 51 (13). HR-MS: 249.0830 (M^+, $C_{13}H_{15}NO_2S^+$; calc. 249.0824). Enantiomer separation by HPLC: *OD-H* column; hexane/i-PrOH 25:1, 0.5 ml/min.; τ_1 0 69, $\tau_2 = 75$ min.

Rearrangement of **25** *to* N-*[(1*S*,2*R*,6*S*)-(bicyclo[4.3.0]non-2-yl)]-4-methylbenzenesulfonamide* (**17**). FC (SiO_2; AcOEt/pentane 1:9): 35%. Colorless crystals. M.p. 112 – 114°. $[\alpha]_D^{20} = +24.0$ ($c = 1.67$, $CHCl_3$) for 68% ee. IR ($CHCl_3$): 3541*w*, 3389*m*, 3272*w*, 3017*s*, 2934*s*, 2296*w*, 1605*w*, 1342*m*, 1144*s*, 1093*m*, 921*w*, 760*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.26 – 1.59 (*m*, 10 H); 1.82 – 1.96 (*m*, 1 H); 1.99 – 2.12 (*m*, 1 H); 2.43 (*s*, 3 H); 3.46 – 3.59 (*m*, 1 H); 4.56 (*d*, *J* = 8.2, 1 H); 7.28 (*d*, *J* = 8.2, 2 H); 7.76 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR (400 MHz, $CDCl_3$): 20.9 (*t*); 21.5 (*t*); 24.6 (*t*); 26.5 (*t*); 27.8 (*t*); 40.0 (*d*); 44.4 (*d*); 53.6 (*d*); 127.0 (*d*); 129.6 (*d*); 138.4 (*s*); 143.0 (*s*). MS: 293 (M^+, 20), 250 (27), 155 (50), 149 (41), 139 (15), 138 (95), 123 (14), 122 (40), 109 (10), 95 (15), 93 (20), 92 (15), 91 (100), 81 (21), 80 (13), 79 (23), 77 (11), 69 (20), 67 (30), 65 (28), 57 (37), 55 (30), HR MS: 293.1449 (M^+, $C_{16}H_{23}NO_2S^+$; calc. 293.1450). Enantiomer separation by HPLC: *OD-H* column; hexane/i-PrOH 25:1, 0.5 ml/min; $\tau_1 = 35$, $\tau_2 = 41$ min.

Rearrangement of **13** to N-*[(1*S*,2*R*,6*S*)-(bicyclo[4.4.0]decyl)]-4-methylbenzenesulfonamide* (**14**). FC (SiO_2, AcOEt/pentane 1:9): 15%. M.p. 114 – 116°. $[\alpha]_D^{20} = +16.0$ ($c = 0.5$, $CHCl_3$) for 47% ee. IR ($CHCl_3$): 3013*s*, 2928*m*, 1220*m*, 1206*s*, 1157*m*, 794*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.22 – 1.71 (*m*, 14 H); 2.43 (*s*, 3 H); 3.23 – 3.25 (*m*, 1 H); 4.44 (br. *d*, *J* = 8.3, 1 H); 7.28 (*d*, *J* = 8.1, 2 H); 7.75 (*d*, *J* = 8.1, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.3 (*t*); 21.1 (*t*); 21.5 (*q*); 24.1 (*t*); 25.2 (*t*); 26.1 (*t*); 27.8 (*t*); 31.7 (*t*); 36.2 (*d*); 41.1 (*d*); 56.3 (*d*); 126.9 (*d*); 129.6 (*d*); 139.5 (*s*); 143.1 (*s*). MS: 307 (11, M^+), 264(13), 210 (11), 155 (31), 152 (79), 136 (48), 135 (19), 107 (12), 93 (15), 92 (12), 91 (100), 81 (18), 79 (15), 69 (10), 67 (36), 65 (25), 56 (30), 55 (24). HR MS: 307.1589 (M^+, $C_{17}H_{25}NO_2S^+$; calc. 307.1606).

4. *Ligands for Desymmetrization of Aziridines. (–)-Sparteine* (**1**). (–)-Sparteine · H_2SO_4 · 5 H_2O (*Fluka*) was treated with aq. NaOH soln., the mixture was extracted with Et_2O, the extract was distilled, and the product stored under Ar at – 78°. (S)*-(–)-1-[(1-Methylpyrrolidin-2-yl)methyl]piperidine* (**26**) was purchased from *Aldrich* and used without purification. N,N′*-Bis[(*R*)-1-phenylethyl-(*R,R′*)-[2,2′]bipyrrolidinyl* (**27**) was synthesized according to [30]. *(1*R*,2*S*)-1-Methoxy-*N,N*-dimethyl-1-phenylpropan-2-amine* (**28**) was prepared from (1*R*,2*S*)-*N*-methylephedrine according to [31]. *1-((1*R*,2*R*)-1,2-Dimethoxy-2-phenylethyl)benzene* (**29**) was

prepared according to [32]. The synthesis of *(–)-(1*R*,2*S*)-1-(methoxymethoxy)-*N,N*-dimethyl-1-phenyl propan-2-amine* (**30**) has been described in a previous communication [33].

*(1*R*,3*R*,4*S*)-2-((*S*)-1-Phenylethyl)-3-(pyrrolidin-1-ylmethyl)-2-azabicyclo[2.2.1]hept-5-ene* (**31**) [34]. To [(1*R*,3*R*,4*S*)-2-((*S*)-1-phenylethyl)-2-azabicyclo[2.2.1]-hept-5-en-3-yl](pyrrolidin-1-yl)methanone [35] (2.00 g, 6.75 mmol) in THF (50 ml) was added $LiAlH_4$ (324 mg, 8.10 mmol), and the suspension was heated to reflux for 12 h. The mixture was hydrolyzed at 0° with H_2O (5.0 ml) and 10% aq. NaOH soln. (5.0 ml). After extraction with Et_2O (3 × 30 ml), the org. layer was dried ($MgSO_4$), filtered, and evaporated to afford **31** (1.49 g, 78%) as colorless crystals. M.p. 93 – 95°. $[\alpha]_D^{20} = +74.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 2971*m*, 1453*w*, 1261*w*, 1097*w*, 719*m*, 670*m*, 479*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.39 (*d*, *J* = 6.6, 3 H); 1.41 – 1.44 (*m*, 1 H); 1.57 (br. *s*, 4 H); 1.65 – 1.67 (*m*, 2 H); 1.76 (*dd*, *J* = 11, 2.2, 1 H); 2.18 – 2.32 (*m*, 2 H); 2.97 (br. *s*, 1 H); 3.00 (*q*, *J* = 6.6, 1 H); 4.15 (*s*, 1 H); 6.16 (*dd*, *J* = 5.6, 1.6, 1 H); 6.43 (*m*, 1 H); 7.27 – 7.32 (*m*, 5 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.0 (*q*); 23.2 (*t*); 44.9 (*t*); 46.1 (*d*); 54.4 (*t*); 61.8 (*d*); 61.9 (*t*); 63.0 (*d*); 63.7 (*d*); 127.2 (*d*); 128.2 (*d*); 128.5 (*d*); 131.5 (*d*); 137.2 (*d*); 145.7 (*s*). MS: 282 (< 1, M^+), 198 (35), 105 (100), 94 (53), 84 (57). HR MS: 282.2094 (M^+, $C_{10}H_{26}N_2^+$; calc. 282.2096).

5. *Synthesis and Rearrangement of 1,6-Dideuterio-7-[(4-methylphenyl)sulfonyl]-7-azabicyclo[4.1.0]heptane* (**20**). *1,2-Dibromocyclohexene* (**19**) [16]. To KOH (19.6 g, 0.30 mol) in MeOH (120 ml) was dropwise added 1,2-dibromo-1-chlorocyclohexane (55.3 g, 0.2 mol) in refluxing MeOH (100 ml). After 3 h of reflux, the mixture was cooled to r.t., neutralized with 50% HCl, and extracted with CH_2Cl_2 (3 × 100 ml). The combined org. layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Recrystallization of the residue from pentane afforded **19** as a colorless solid (35.2 g, 73%). M.p. 43 – 45°. IR ($CHCl_3$): 3012*s*, 2945*s*, 2864*m*, 2360*m*, 1710*w*, 1635*m*, 1435*m*, 1435*m*, 1116*w*, 1075*w*, 994*s*, 778*m*, 741*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.72 – 1.78 (*m*, 4 H); 2.53 – 2.58 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 24.0 (*t*), 37.2 (*t*); 122.9 (*s*). MS: 242 (36), 240 (74, M^+), 238 (38), 161 (36), 159 (36), 133 (22), 131 (22), 80 (49), 79 (100), 78 (17), 161 (36), 159 (36), 53 (13), 51 (44), 50 (19). HR-MS: 239.9123 ($C_6H_{10}{}^{79}Br_2^+$; calc. 239.9149); 241.9124 ($C_6H_{10}{}^{79}Br^{81}Br^+$; calc. 241.9129).

1,2-Dideuteriocyclohexene (**18**) [16]. To a suspension of Zn (11.0 g, 169 mmol) in H_2O (17 ml) was added, under vigorous stirring, [$CuCl_2$] (0.15M in 5% HCl, 14 ml). When the evolution of HCl gas was terminated, the suspension was filtered. The black residue was washed with acetone (2 ×), D_2O (1 ×), acetone (2 ×), and, finally, Et_2O (2 ×), and was dried *in vacuo* at r.t. for 3 h. This Zn/Cu couple in dyglyme (15 ml), containing D_2O (8.08 g, 404 mmol), was added to **19** (9.70 g, 40.4 mmol). The mixture was stirred at 80° for 12 h, and was then distilled at atmospheric pressure. The fraction boiling at 72° was collected: 1.99 g (59%). B.p. 72°. IR ($CHCl_3$): 2926*s*, 2837*m*, 2673*m*, 2259*w*, 1625*w*, 1438*m*, 1223*w*, 1131*w*, 895*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.60 – 1.63 (*m*, 4 H); 1.97 – 2.00 (*m*, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.6 (*t*); 25.0 (*t*); 126.7 (*dt*, $J(^2H,^{13}C) = 95.8$).

1,6-Dideuterio-7-[(4-methylphenyl)sulfonyl]-7-aza-bicyclo[4.1.0]heptane (**20**). To [$Cu(OTf)_2$] (22 mg, 0.60 mmol) in anh. MeCN (2.0 ml, dried over molecular sieves 4 Å) was added **18** (1.50 g, 17.9 mmol) in MeCN (1.0 ml). The suspension was stirred for 30 min. at r.t. Then, TsN=IPh (2.23 g, 6.00 mmol) was added slowly, and the mixture was stirred at r.t. for 90 min. The mixture was filtered over SiO_2, eluting with MeCN (300 ml): 1.24 g (81%). M.p. 64 – 66°. IR ($CHCl_3$): 3020*w*, 2945*w*, 2857*w*, 1599*w*, 1596m, 1434w, 1319w, 1219*s*, 1202*m*, 1155*m*, 109*m*, 960*m*, 815*w*, 746*s*, 708*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.19 – 1.28 (*m*, 2 H); 1.37 – 1.44 (*m*, 2 H); 1.77 – 1.80 (*m*, 4 H); 2.45 (*s*, 3 H); 7.33 (*d*, *J* = 8.0, 2 H); 7.82 (*d*, *J* = 8.0, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.4 (*t*); 21.6 (*q*); 22.7 (*t*); 39.4 (*dt*, $J(^2H,^{13}C) = 102.6$); 127.6 (*d*); 129.5 (*d*); 135.9 (*s*); 143.9 (*s*). MS: 253 (< 1, M^+); 98 (100), 97 (25), 91 (20), 71 (14), 70 (37), 65 (11). HR-MS: 253.1135 ($C_{13}{}^1H_{15}{}^2HNO_2S^+$; calc. 253.1106).

N-*(1-Deuteriocyclohex-2-en-1-yl)-4-methylbenzenesulfonamide* (**23**). To *s*-BuLi (1.3M in hexane, 0.91 ml, 1.28 mmol) in Et_2O (2.0 ml) at – 78° was added dropwise and under Ar (–)-sparteine (**1**, 2.78 g, 1.18 mmol) in Et_2O (1.0 ml) over 10 min. After 1.3 h of stirring at this temp., **20** (100 mg, 0.39 mmol) was added. The temp. was maintained at – 78° for 3.5 h. Then, the mixture was allowed to reach 10°, and stirring was continued at this temp. for an additional 3.5 h. The mixture was hydrolyzed with sat. aq. NH_4Cl soln. (10 ml), the layers were separated, and the aq. layer was extracted with Et_2O (3 × 10 ml). The combined org. layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by FC (SiO_2, AcOEt/pentane 1:9): 10 mg (10%). IR ($CHCl_3$): 3278*m*, 3021*w*, 2925*m*, 2856*w*, 1720*m*, 1598*w*, 1224*w*, 1206*s*, 1157*s*, 788*s*, 757*s*, 717*w*, 672*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.24 – 1.28 (*m*, 2 H); 1.38 – 1.42 (*m*, 2 H); 1.61 – 1.93 (*m*, 2 H); 2.05 – 2.18 (*m*, 2 H); 2.44 (*s*, 3 H); 4.38 (br. *s*, 1 H); 5.35 (*m*, 1 H); 5.76 – 5.79 (*m*, 1 H); 7.30 – 7.32 (*d*, *J* = 7.9, 2 H); 7.76 – 7.78 (*d*, *J* = 7.9, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.2 (*t*); 21.5 (*q*); 24.4 (*t*); 30.1 (*t*); 126.87 (*d*); 126.91 (*d*); 129.7 (*d*); 131.7 (*d*); 138.3 (*s*); 143.2 (*s*). MS: 252 (3, M^+), 225 (21), 224 (35), 189 (18), 188 (32), 187 (14), 155 (61), 149 (10), 139 (12), 106 812), 98 (25), 97 (50), 92 (23), 91 (100), 83 (13), 82 (15), 81 (17), 71 (10), 70 (16), 69 (34), 65 (24), 57 (14), 55 (13). HR MS: 252.1032 ($C_{13}{}^1H_{16}{}^2HNO_2S^+$; calc. 252.1043).

6. *Crystal Structure Determination of (*S*)-**4**, (2*R*)-**16** and (2*R*)-**17**.* Cell dimensions and intensities were measured at 200 K on a *Stoe IPDS* diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Data were corrected for *Lorentz* and polarization effects, and for absorption. The structures were solved by direct methods (SIR-97) [36], and all other calculations were performed with the XTAL system [37] and ORTEP [38] programs. All crystals used for X-ray diffraction were subjected to HPLC analysis after the data collections. For compound **4**, both molecules of the asymmetric unit differ by the orientation of the Ts group (rotation about the N–S bond), with dihedral angles C(1)–N–S–C(8) = 58.5(4) and – 72.8(5)° for molecules *a* and *b*, resp.). The three compounds show H-bond interactions between the NH fragment and an O-atom of the sulfone of a neighboring molecule.

Table 2. *X-Ray Crystal Data, Parameters, and Structure Refinements*

	(3*S*)-**4**	(2*R*)-**16**	(2*R*)-**17**
Formula	$C_{14}H_{17}NO_2S$	$C_{15}H_{21}NO_2S$	$C_{16}H_{23}NO_2S$
M_w	263.4	279.4	293.5
Solvent of crystallization	Hexane	Pentane	Octane
Crystal size [mm]	0.16 × 0.17 × 0.24	0.08 × 0.24 × 0.25	0.14 × 0.19 × 0.20
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	10.0223(9)	6.3246(3)	6.3943(3)
b [Å]	12.4263(8)	10.9438(5)	11.1347(8)
c [Å]	11.1608(11)	20.9285(13)	21.6943(11)
β [°]	106.653(10)	90	90
V [Å^3]	1331.7(2)	1448.6(1)	1544.6(2)
Z	4	4	4
D_x [g cm^{-3}]	1.314	1.281	1.262
μ (MoK_α) [mm^{-1}]	0.237	0.222	0.211
$T_{\min}$, $T_{\max}$	0.9525, 0.9728	0.9463, 0.9826	0.9622, 0.9730
$((\sin\theta)/\lambda)_{\max}$ [Å^{-1}]	0.664	0.661	0.613
Reflections measured	20438	22645	19300
Independent reflcections	6369	3442	2987
Observed reflcections	4216	1947	1624
Observation criterion	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$
Refinement (on F)	Full matrix	Full matrix	Full matrix
No. of parameters	331	227	185
Weighting scheme p[a])	0.00015	0.0002	0.0004
Maximum Δ/σ	$0.31 \cdot 10^{-3}$	$0.25 \cdot 10^{-3}$	$0.40 \cdot 10^{-3}$
Max. and min. $\Delta\varrho$[e Å^{-3}]	0.42, – 0.48	0.25, – 0.24	0.42, – 0.47
Flack parameter x	– 0.03(12)	– 0.01(12)	– 0.06(20)
S[b])	1.64	1.29	1.67
R[c]), ωR[d])	0.033, 0.033	0.031, 0.031	0.043, 0.046

[a]) $\omega = /[\sigma^2(F_o) + p(F_o)^2]$. [b]) $S = [\Sigma\{((F_o - F_c)/\sigma(F_o))^2\}/(N_{\mathrm{ref}} - N_{\mathrm{var}})]^{1/2}$. [c]) $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.
[d]) $\omega R = [\Sigma(\omega|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

CCDC-211710, -211711, and -211712 contain supplementary crystallographic data for compounds (3*S*)-**4**, (2*R*)-**16**, and (2*R*)-**17**, respectively. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK (fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

[1] J. K. Crandall, M. Apparu, *Org. React.* **1983**, *29*, 345.

[2] a) D. M. Hodgson, A. R. Gibbs, G. P. Lee, *Tetrahedron* **1996**, *52*, 14261; D. M. Hodgson, A. R. Gibbs, M. G. B. Drew, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3579; b) S. E. Denmark, P. A. Barsani, K. T. Wong, R. A. Stavenger *J. Org. Chem.* **1998**, *63*, 2428; c) S. K. Bertillson, M. J. Södergren, P. G. Andersson, *J. Org. Chem.* **2002**, *67*, 1567; A. Magnus, S. K. Bertilsson, P. G. Andersson, *J. Chem. Soc. Rev.* **2002**, *31*, 223; d) H. Ramirez, D. Collum, *J. Am. Chem. Soc.* **1999**, *121*, 1114; e) K. M. Morgan, S. Gronert, *J. Org. Chem.* **2000**, *65*, 1461.

[3] A. C. Cope, B. D. Tiffany, *J. Am. Chem. Soc.* **1951**, *73*, 4158; K. M. Morgan, J. J. Gajewski, *J. Org. Chem.* **1996**, *61*, 820.

[4] D. M. Hodgson, E. Gras, *Synthesis* **2000**, 1625.

[5] D. Hoppe, F. Hintze, P. Tebben, *Angew. Chem., Int. Ed.* **1990**, *29*, 1422; D. Hoppe, T. Hense, *Angew. Chem., Int. Ed.* **1977**, *36*, 2282.

[6] a) D. M. Hodgson, G. P. Lee, R. E. Marriott, A. J. Thompson, R. Wisedale, J. Witherington, *J. Chem. Soc., Perkin Trans. 1* **1998**, 2151; b) D. M. Hodgson, C. R. Maxwell, T. J. Miles, E. Paruch, M. A. H. Stent, I. R. Matthews, F. X. Wilson, J. Witherington, *Angew. Chem., Int. Ed.* **2002**, *41*, 4313; c) D. M. Hodgson, E. Gras, *Angew. Chem., Int. Ed.* **2002**, *41,* 2376; d) D. M. Hodgson, I. D. Cameron, M. Christlieb, R. Green, G. P. Lee, L. A. Robinson, *J. Chem. Soc., Perkin Trans 1* **2001**, 2161; e) D. M. Hodgson, L. A. Robinson, M. L. Jones, *Tetrahedron Lett.* **1999**, *40*, 8637; f) D. M. Hodgson, C. R. Maxwell, I. R. Matthews, *Tetrahedron: Asymmetry* **1999**, *10*, 1847.

[7] P. O'Brien, C. D. Pilgram, *Tetrahedron Lett.* **1999**, *40*, 8427; P. O'Brien, C. D. Pilgram, *Org. Biomol. Chem.* **2003**, *1*, 523; P. O'Brien, C. M. Rosser, D. Caine, *Tetrahedron* **2003**, *59*, 9779.

[8] P. Müller, P. Nury, *Helv. Chim. Acta* **2001**, *84*, 662.

[9] P. O'Brien (University of York), personal communication, April 2003.

[10] A. Mordini, F. Russo, M. Valacchi, L. Zani, A. Degl'Innocenti, G. Reginato, *Tetrahedron* **2002**, *58*, 7153.

[11] T. Katsuki (Kyushu University, Fukuoka), personal communication, October 2002.

[12] Z. da Zhang, R. Scheffold, *Helv. Chim. Acta* **1993**, *76*, 2602.

[13] H. Brown, A. Felber, G. Kresse, A. Retter, F. P. Schmidtchen, *Tetrahedron* **1991**, *47*, 3313.

[14] M. A. Dyadchenko, V. I. Mel'nikova, K. K. Pivniskii, *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *58*, 1891.

[15] C. Djerassi, J. Staunton, *J. Am. Chem. Soc.* **1961**, *83*, 736.

[16] K. Voigt, A. de Mejere, *Eur. J. Chem.* **1998**, 1521.

[17] L. M. Stephenson, R. V. Gemmer, S. P. Current, *J. Org. Chem.* **1977**, *42*, 212.

[18] W. H. Saunders, A. F. Cockrill, 'Mechanism of Elimination Reactions', John Wiley & Sons, New York, 1973.

[19] D. Pattersen, M. Amedjkouh, P. Ahlberg, *Tetrahedron* **2002**, *58*, 4669; D. Pettersen, M. Amedjkouh, S. O. Nilsson Lill, P. Ahlberg, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1397; S. O. Nillson Lill, M. Amdjkouh, P. Ahlberg, *J. Chem. Soc., Perkin Trans 1* **2001**, 3054; M. Amedjkouh, D. Pettersen, S. O. Nilsson Lill, O. Davidsson, P. Ahlberg, *Chem. – Eur. J.* **2001**, *7*, 4368; R. I. Olsson; P. Ahlberg, *Tetrahedron: Asymmetry* **1999**, *10*, 3991; P. I. Avidsson, P. Ahlberg, G. Hilmersson, *Chem. – Eur. J.* **1999**, *5*, 1348.

[20] P. Müller, P. Nury, *Helv. Chim. Acta* **2001**, *84*, 662.

[21] Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett.* **1975**, 361.

[22] P. Müller, C. Baud, Y. Jacquier, *Can. J. Chem.* **1998**, *76*, 738.

[23] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, *116*, 2742.

[24] J. Jeong, B. S. I. Tao, H. Henniges, K. B. Sharpless, *J. Am. Chem. Soc.* **1998**, *120*, 6844.

[25] P. Müller, C. Baud, Y. Jacquier, *Tetrahedron* **1996**, *52*, 1543.

[26] B. Ziperer, K.-H. Mueller, B. Gallenkampf, R. Hildebrand, M. Fletschinger, *Chem. Ber.* **1998**, *121*, 757.

[27] J.-P. Mahy, G. Bedi, P. Battioni, D. Mansuy, *J. Chem. Soc., Perkin Trans. 2* **1988**, 1515.

[28] K. J. Shea, J.-S. Kim, *J. Am. Chem. Soc.* **1992**, *114*, 3044; L. Skattebol, S. Solomon, *J. Org. Chem.* **1964**, *29*, 1976; P. D. Gardner, M. Narayana, *J. Org. Chem.* **1961**, *26*, 3518.

[29] D. Y. Kim, H. S. Kim, Y. J. Choi, J. Y. Mang, K. Lee, *Synth. Commun.* **2001**, *31*, 2463.

[30] A. Alexakis, A. Tomassini, C. Chouillet, G. Bernardinelli, *Angew. Chem., Int. Ed.* **2000**, *39*, 4093.

[31] S. G. Davies, S. Coole, C. L. Goodfellow, K. H. Sulton, D. Middlemiss, A. Naylor, *Tetrahedron: Asymmetry* **1990**, *1*, 817.

[32] D. Ammurio, K. Khan, E. P. Kuendig, *J. Org. Chem.* **1996**, *61*, 2258.

[33] P. Müller, P. Nury, G. Bernardinelli, *Eur. J. Org. Chem.* **2001**, 4137.

[34] V. Vecchietti, A. Giordani, G. Giardina, G. D. Clarke, *J. Med. Chem.* **1991**, *34*, 397.
[35] S. A. Modin, P. G. Andersson, *J. Org. Chem.* **2000**, *65*, 6736.
[36] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[37] XTAL3.2 (User's Manual), Eds. S. R. Hall, H. D. Flack, J.-M. Stewart, Universities of Western Australia and Maryland, 1992.
[38] C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Received July 11, 2003