Desymmetrization of *meso-N*-Sulfonylaziridines with Chiral Nonracemic Nucleophiles and Bases

by **Paul Müller*** and **Patrice Nury**

Department of Organic Chemistry, University of Geneva 30, Quai Ernest Ansermet, CH-1211 Geneva 4

The cyclohexene-derived aziridine 7-tosyl-7-azabicyclo[4.1.0]heptane (**1**) reacts with *Grignard* reagents in the presence of chiral nonracemic Cu-catalysts to afford sulfonamides **3a**–**e** (*Scheme 3*) in up to 91% ee under optimized conditions (*Table 2*). No activation of the aziridine by *Lewis* acids is required. The reaction may be extended to other bicyclic *N*-sulfonylated aziridines, but aziridines derived from acyclic olefins, cyclooctene, and trinorbornene are unreactive under standard conditions (*Scheme 5*). Exposure of **1** to *s*-BuLi in the presence of (–)-sparteine (2.8 equiv.) affords the allylic sulfonamide **31** in 35% yield and 39% ee (*Scheme 6*). Under the same conditions, the aziridines **33** and **35** yield products **34** and **36** derived from intramolecular carbenoid insertion with 75 and 43% ee, respectively.

Introduction. – Aziridines are the N-analogues of epoxides, and as such, are attractive intermediates for a variety of transformations affording N-containing products [1]. In this context, the synthesis of chiral nonracemic aziridines is of particular interest. However, although chiral aziridines are accessible *via* asymmetric aziridination of olefins [2], the methods currently available are limited. Alternatively, optically active products derived from ring opening of achiral aziridines are, in principle, accessible *via* their enantioselective desymmetrization, in analogy with the widely and successfully applied desymmetrization of achiral epoxides [3]. This latter reaction may be effected *via* α-deprotonation [4], β-deprotonation [5], or *via* nucleophilic ring opening under stoichiometric [6] and catalytic conditions [7]. Several procedures for selective ring opening of aziridines by nucleophilic substitution are known. *N*-Alkyl- or *N*-(arylalkyl)aziridines undergo ring opening in the presence of catalytic amounts of lanthanide ions, in particular Yb^{III} [8], and react with aromatic amines in the presence of Sn^{II} or Cu^{II} catalysts [9]. Enantioselective opening of *N*-alkylaziridines with up to 94% ee has been reported for their reaction with azidotrimethylsilane (Me_3SiN_3) and a tridentate *Schiff*-base chromium complex [10]. A catalytic method involving thiols in the presence of $ZnEt_2$ and an optically active tartrate for desymmetrization of *N*-acylated aziridines has recently been published [11]. Ring opening of aziridines by organometallic reagents, in turn, has been known since 1985, when *Eis* and *Ganem* reported the opening of *N*-alkylaziridines by organocuprates under stoichiometric conditions in the presence of BF_3 [12]. Subsequently, *Baldwin et al.* found that *N*-sulfonated aziridines do not require BF_3 to react with organocuprates [13], and several applications of this observation appeared [14][15], including achiral opening of *N*-phosphinylaziridines with organocuprates [16].

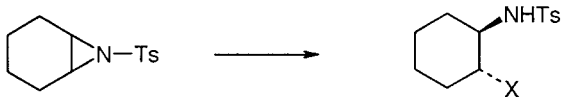
In the context of our ongoing research on catalytic aziridination of olefins [2a][17], a certain number of chiral and *meso-N*-sulfonylaziridines were synthesized *via* Rh^{II}-

catalyzed reaction of olefins with PhI=NTs. Surprisingly, however, when very electron-rich olefins were used as substrates, *N*-sulfonylated pyrrolidines were isolated; these were formally derived by ring opening of the putative intermediate aziridines to dipolar species which, apparently, underwent cycloaddition to the olefin present in excess. The aziridine opening was attributed to the presence of the electrophilic rhodium(II) carboxylate or carboxamidate catalysts. This observation suggested the possibilty of aziridine desymmetrization by chiral Rh^{II} catalysts, and experiments in this direction were initiated. Although the original idea could not be realized, we found, in the course of these investigations, conditions under which desymmetrization of *N*-sulfonated aziridines occurred under catalytic conditions with organometallic reagents in the presence of chiral Cu-complexes [18].

Results. – *Exploratory Experiments for Nucleophilic Ring Opening of Aziridines.* Exploratory experiments with the cyclohexene-derived aziridine 7-tosyl-7-azabicyclo[4.1.0]heptane (**1**) and *Lewis* acid catalysts revealed that rhodium(II) carboxylates are not sufficiently electrophilic to effect ring opening of aliphatic aziridines. Thus, no reaction occurred when **1** was exposed to nucleophiles such as azidotrimethylsilane (Me_3SiN_3), trimethylsilanecarbonitrile, aniline, *etc.* in refluxing CH_2Cl_2 in the presence of $[Rh_2(OAc)_4]$. NaN_3 in DMF was effective at room temperature and in refluxing MeCN, but addition of $[Rh_2(OAc)_4]$ had no catalytic effect (*Table 1*). Me_3SiN_3 in conjunction with $[Cu(acac)_2]$ (Hacac = pentane-2,4-dione) or [Zn(tartrato)] afforded ring-opened **2a** [19] in refluxing MeCN, but the reaction required 7 to 12 d to go to completion. Similarily, the [Cr(salen)] complex (H_2salen = bis(salicylidene)ethylenediamine) of *Jacobsen* and co-workers [7d,e] [20] was not effective with Me_3SiN_3. These results indicated that the presence of the strongly electron-attracting sulfonate group at the N-atom of **1** decreases its basicity to such an extent that association with the electrophilic catalyst was ineffective for opening of the aziridine ring. This hypothesis is supported by the recent observation of *Jacobsen* and coworkers [10] that the more basic *N*-benzyl-substituted aziridines react with Me_3SiN_3 with a chiral [Cr(*Schiff* base)] catalyst at low temperature and with excellent enantioselectivity. Nevertheless, **1** did react with Me_3SiN_3 and $[TiCl_2(O^iPr)_2]$, but the reaction took place *via* chloride attack to afford **2b**. Exposure of **1** to MeMgBr in the absence of catalyst resulted in formation of the bromide **2c** [21], suggesting activation of the aziridine by Mg^{II}. That Mg ions may activate **1** was further demonstrated by conversion of **1** to **2c** with $MgBr_2$. The possibility of effecting aziridine opening with Mg complexes was not further explored at that time. However, addition of 10% of $[Cu(acac)_2]$ to MeMgBr resulted in nucleophilic attack by the organometallic reagent, and **3a** was obtained in 85% yield.

Cu-Catalyzed Desymmetrization of **1** *with MeMgBr.* The enantioselectivity of the reaction was investigated with several chiral catalysts (see **4**–**17**; *Fig.*), which were prepared according to literature procedures or in analogy to reported methods (for references to **4**–**14**, see *Exper. Part*). The synthesis of phosphoramidite **13** derived from 8,8′-binol ([1,1′-binaphthalene]-8,8′-diol) is reported elsewhere [22]. The dihydrooxazole ligand **16** was synthesized by reaction of (4*S*)-4,5-dihydro-4-isopropyl-α,α-dimethyloxazole-2-methanol (**19**) with *in situ* prepared phosphorochloridite **18** [23] (*Scheme 2*). Racemic biphenanthrenediol **20** was prepared by oxydative coupling of phenanthren-9-ol with $[CuCl_2]$ [24] or with $[CuCl(OH)]\cdot$TMEDA (*N*,*N*,*N*′,*N*′-

Scheme 1[a])



1

2a X = N_3
b X = Cl
c X = Br
3a X = Me

[a]) The relative configuration of **2a**–**c** and **3a** is shown.

tetramethylethylenediamine) [25]. The enantiomers of **20** were separated either *via* the cyclic phosphoramidite, derived from (−)-(*S*)-α-methylbenzylamine followed by reduction with $LiAlH_4$ [25], or according to the procedure described by *Toda* and *Tanaka* [26]. The (*S*)-enantiomer of **20** was treated with diisopropylphosphoramidous dichloride (**21**) [27] to afford the phosphoramidite **17**.

Table 1. *Electrophilic Catalysis in the Ring Opening of* **1**

Nucleophile	Catalyst	Solvent	Temp., time	Product	Yield/%
NaN_3, 1.2 equiv.	–	MeCN	Reflux, 24 h	**2a**	89
NaN_3, 1.2 equiv.	$[Rh_2(OAc)_4]$, 10%	MeCN	Reflux, 24 h	**2a**	85
Me_3SiN_3, 1.2 equiv.	$[Cu(acac)_2]$, 10%	MeCN	Reflux, 12 d	**2a**	60
Me_3SiN_3, 4.0 equiv.	$[Cu(acac)_2]$, 20%	MeCN	Reflux, 7 d	**2a**	74
Me_3SiSN_3, 1.2 equiv.	[Zn(tartrato], 10%	MeCN	Reflux, 12 d	**2a**	65
Me_3SiN_3, 4.0 equiv.	[Zn(tartrato)], 20%	MeCN	Reflux, 7 d	**2a**	81
Me_3SiN_3, 1.2 equiv.	$[Zn(Et)_2]$, 10%	CH_2Cl_2	0°, 7 d	**2a**	58
Me_3SiN_3, 1.2 equiv.	$[TiCl_2(O\text{-}^iPr)_4]$, 10%	CH_2Cl_2	0°, 2 d	**2b**	20
Me_3SiN_3, 1.2 equiv.	$[TiCl_2(O\text{-}^iPr)_4]$, 50%	CH_2Cl_2	0°, 2 d	**2b**	88
MeMgBr 1.2 equiv.	–	THF	0°, 6 h	**2c**	91
$MgBr_2$, 1.0 equiv.	–	THF	0°, 24 h	**2c**	82
MeMgBr, 1.2 equiv.	$[Cu(acac)_2]$, 10%	THF	0°, 1 h	**2d**	85

Aziridine opening was effected either with the isolable Cu complexes (*Method A*), or by preparing the catalysts *in situ* by addition of 0.2 equiv. of the ligand of interest to 0.1 equiv. of $[Cu(OTf)_2]$ (*Method B*). The desymmetrizations were carried out by addition of the organometallic reagent (1.0 equiv.) in THF at 0° to a THF solution containing the aziridine **1** and the catalyst with a 10:1 substrate/catalyst ratio. *Table 2* summarizes the principal results. The effect of solvent, temperature, and origin of the organometallic reagent has been reported in the preliminary communication [18]. The results obtained with still other, less satisfactory ligands, will be reported elsewhere [28].

Yield and enantioselectivity of the reaction depended not only upon the ligand, but also upon the catalyst concentration, the counterion of the organometallic reagent (MgX^+, Li^+), and the solvent [18]. Under standard conditions, the highest ee of 79% resulted with **16**. The reaction conditions were, however, optimized with **8**, which is more readily accessible, and the ee increased from 55% under standard conditions to 91% (in THF with 30% of catalyst, addition of MeMgBr within 10 min). The principal

Scheme 2

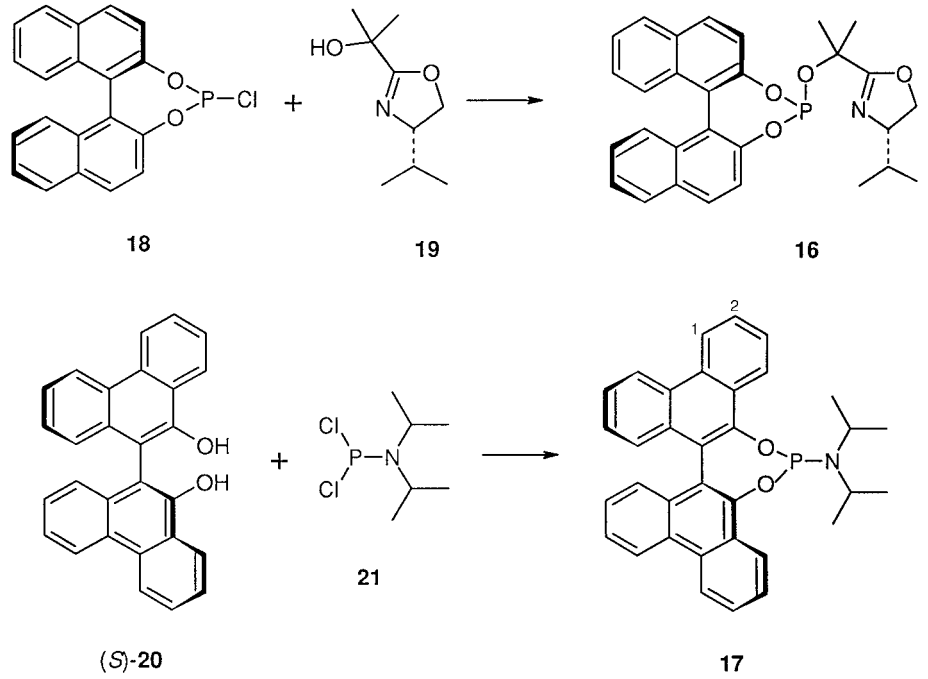


Table 2. *Desymmetrization of Aziridine* **1** *to* **3a** *with MeMgBr*[a])

Catalyst	*Method*	Time/h	Yield/%	ee/%[b]	Absolute configuration
[$Cu(acac_2$]	*A*	1.0	85	–	–
4	*B*	2.0	73	52	(1*S*,2*S*)
5	*B*	2.0	84	29	(1*S*,2*S*)
6	*A*	2.0	71	13	(1*S*,2*S*)
7	*A*	2.0	75	0	–
8	*A*	2.0	89	55	(1*S*,2*S*)
8 (30%)[c])	*A*	1.5	52	91	(1*S*,2*S*)
9a	*A*	1.5	89	28	(1*S*,2*S*)
9b	*A*	3.0	75	12	(1*S*,2*S*)
10	*A*	1.5	78	13	(1*S*,2*S*)
10	*A*	2.0	65	50	(1*S*,2*S*)
12	*B*	2.0	73	31	(1*R*,2*R*)
13	*B*	1.0	64	42	(1*S*,2*S*)
14	*A*	1.5	78	12	(1*R*,2*R*)
15	*B*	2.5	81	21	(1*S*,2*S*)
16	*B*	2.5	59	79	(1*R*,2*R*)
17	*B*	1.5	69	49	(1*S*,2*S*)

[a]) Conditions: MeMgBr (0.60 ml, 1.4M in THF/toluene), added dropwise to **1** (200 mg, 0.80 mmol) and catalyst (0.080 mmol) in THF (2.0 ml) at 0°. [b]) Determined by HPLC (*Chiracel OD H* column, hexane/^{i}PrOH 9 : 1). [c]) Optimized conditions [18].

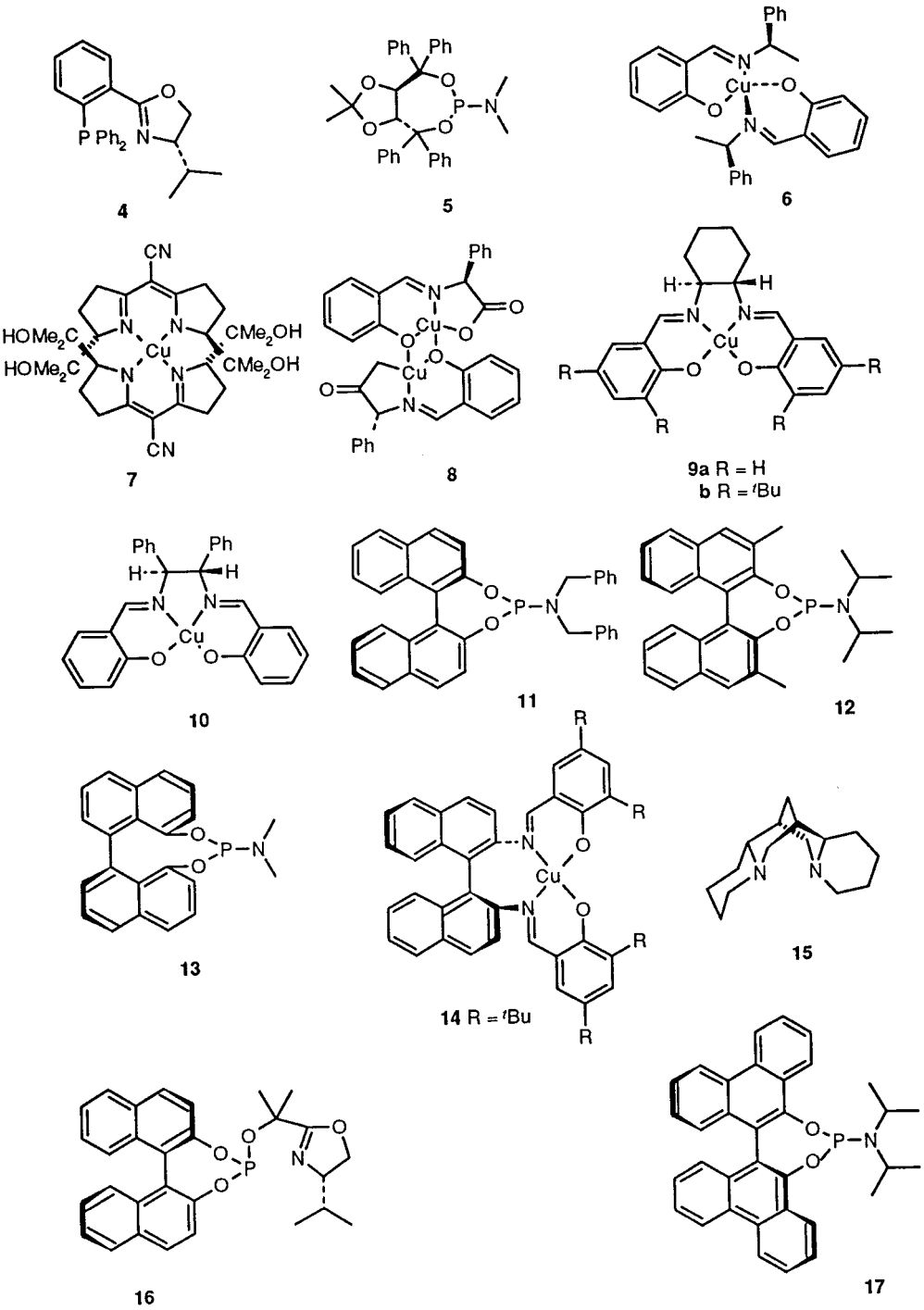


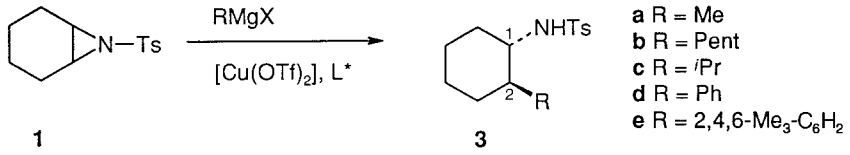
Figure. *Catalysts and ligands*

side reaction was halide attack, leading to **2b** or **2c**, when MeMgCl or MeMgBr, respectively, was used.

Desymmetrization of **1** *with other* Grignard *Reagents.* Variation of the structure of the organometallic reagent was examined under standard conditions. Ligand **8** was used in all cases, but, for some reagents, other ligands were also tested (*Table 3*). No ring opening occurred with HC≡CMgBr, H_2C=CHMgBr and H_2C=$CHCH_2$MgBr, and ^{t}BuMgBr under standard conditions, but *Grignard* reagents derived from primary and secondary alkyl as well as aryl bromides reacted with acceptable yields (→ **3a**–**e**, see *Scheme 3*). The enantioselectivity was quite variable, however, but was not optimized systematically. Surprisingly, while the MeMgBr opened aziridine **1** in the presence of **8** with a moderate selectivity of 55%, the corresponding reaction with PhMgBr afforded only racemic product. Some induction occurred, however, with PhMgBr and **9b** as catalyst, but the absolute configuration at C(1) of the product was opposite of that obtained with MeMgBr and **9b**. Increased steric hindrance at the benzene ring as exemplified with (mesityl)MgBr (mesityl = 2,4,6-trimethylphenyl) resulted in increased enantioselectivity, which culminated at 72% with **8**. Other catalysts were tried with PhMgBr, but the enantioselectivity was in all cases below 10%.

The absolute configuration of **3a** resulting from the reaction with ligand **8** was determined to be (1*S*,2*S*) by its conversion *via* reductive cleavage [29] to the amine **22** of known absolute configuration [30] (*Scheme 4*). For the phenyl-substituted sulfonamide **3d**, the free amine **23** with (+)-(1*S*,2*R*)-configuration was synthesized

Scheme 3[a])



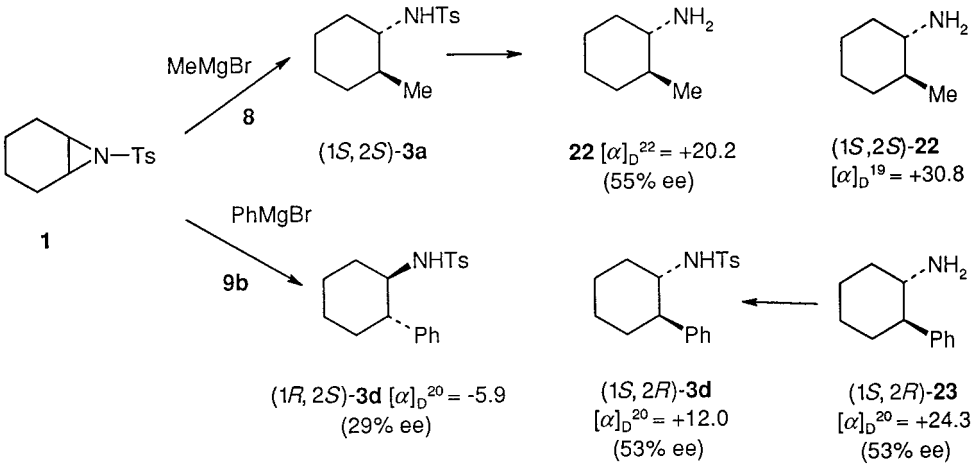
[a]) The relative configuration of **3a**–**e** is shown. The absolute configuration of **3a** is (1*S*,2*S*), and that of **3d** is (1*R*,2*S*) (see *Scheme 4*).

Table 3. *Cu-Catalyzed Ring Opening of* ***1*** *with* Grignard *Reagents*[a])

Nucleophile[b])	Catalyst	Time	Product	Yield/%	ee/%	Absolute configuration
MeMgBr	**8**	2.0 h	**3a**	89	55	(1*S*,2*S*)
MeMgBr	**9b**	2.0 h	**3a**	75	12	(1*S*,2*S*)
(Pentyl)MgBr	**8**	2.0 h	**3b**	75	15	
^{i}PrMgBr	**8**	1.5 h	**3c**	71	21	
PhMgBr	**8**	2.0 h	*rac*-**3d**	80	0	
PhMgBr	**9b**	1.5 h	*ent*-**3d**	75	29	(1*R*,2*S*)
MesMgBr	**5**	3.0 h	**3e**	32	67	
MesMgBr	**8**	3.0 h	**3e**	45	72	
MesMgBr	**9a**	2.5 h	**3e**	48	15	
MesMgBr	**10**	2.5 h	**3e**	63	53	
MesMgBr	**12**	2.5 h	**3e**	55	0	
MesMgBr	**14**	3.0 h	**3e**	28	68	

[a]) Conditions, see *Table 2*. [b]) Mes = 2,4,6-Trimethylphenyl.

Scheme 4

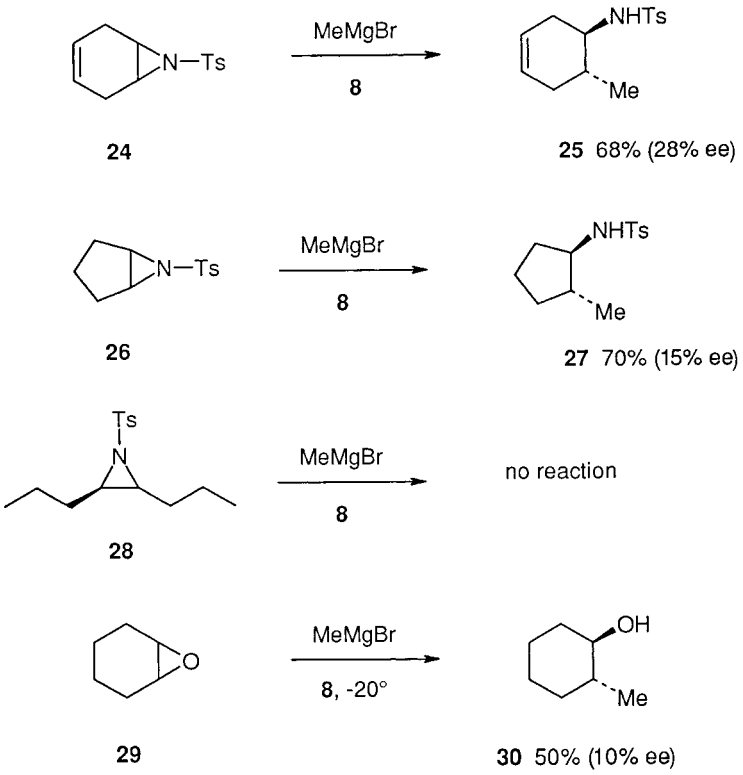


from 2-phenylcyclohexanone and sulfonated with TsCl [31]; comparison of the optical rotation and the HPLC retention time of the thus-obtained sulfonamide revealed (1*S*,2*R*)-**3d** that the phenyl-substituted sulfonamide resulting from reaction of **1** with catalyst **8** was (1*R*,2*S*)-**3d**. The absolute configuration of the other sulfonamides was not determined.

Reaction of Other Substrates with MeMgBr. Likewise, the aziridines **24** and **26** derived from cyclohexa-1,4-diene and cyclopentene, respectively, underwent Cu-catalyzed ring opening in the presence of ligand **8** to afford the sulfonamides **25** and **27**, respectively, with modest enantioselectivities (*Scheme 5*). In contrast, the (*Z*)-oct-4-ene-derived aziridine **28** was unreactive under the conditions of the reactions. Other bicyclic and polycyclic aziridines such as **33** and **35** (*Scheme 6*) were equally unreactive. The catalytic system was also applied to cyclohexene oxide (**29**), which reacted to give *trans*-2-methylcyclohexanol (**30**) [32] in 50% yield, but the enantioselectivity with **8** was poor. The reaction is nevertheless remarkable, because it is catalytic with respect to copper, and, unlike the epoxide opening with organolithium reagents, does not require activation with BF_3 [33]. Chiral heterocuprates have been shown to open **1** to give the corresponding alcohols in at most 3.6% ee [32]. At this time, no attempt has been made towards improvement of the selectivities of the reactions presented in *Scheme 5*.

Sparteine-Mediated Isomerization of N-*Sulfonylaziridines to Allylic Sulfonamides.* The rearrangement of *meso*-epoxides in the presence of chiral bases to chiral allylic alcohols is well-established. However, only a single communication on the analogous isomerization of *N*-acylated aziridines to optically active allylic amines has been published [34]. The reaction occurs in the presence of vitamin B_{12} as catalyst [5b]. It is believed to involve nucleophilic ring opening by the Co^{I} nucleophile to a Co^{III} intermediate, which then undergoes reductive elimination to an allylic amide and Co^{I}. In contrast, *N*-sulfonylated- or *N*-phosphinoylated aziridines reportedly do not rearrange to allylic amines in the presence of lithium amide bases [35].

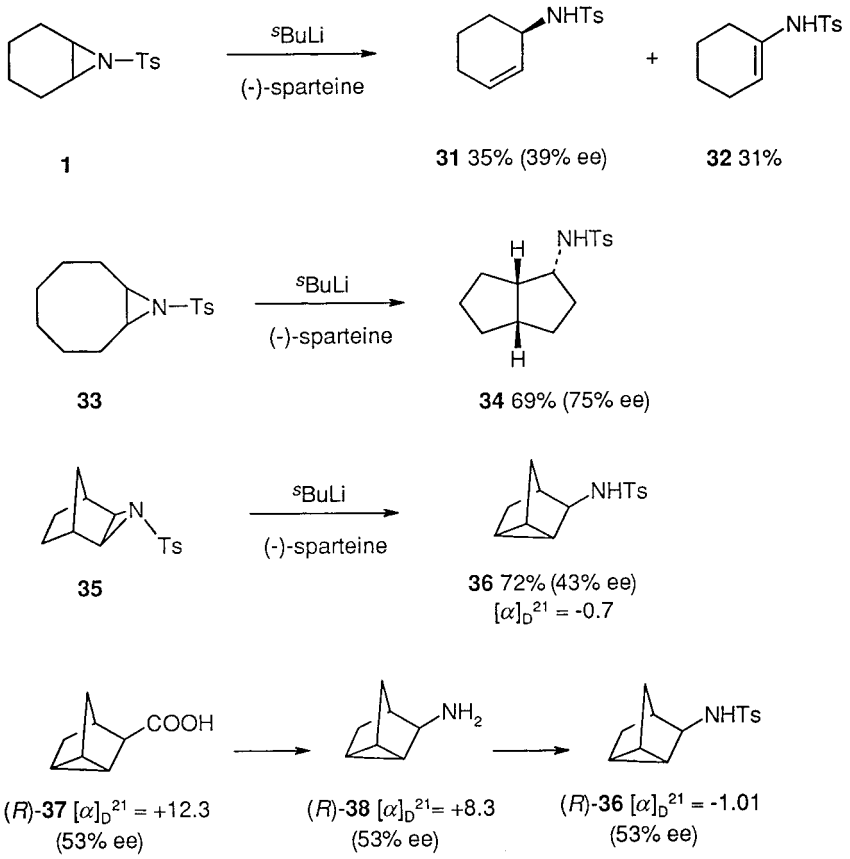
Scheme 5



When **1** was exposed to ^{s}BuLi in the presence of 2.8 equiv. of (−)-sparteine, rearrangement occurred to the allylic *N*-(cyclohex-2-en-1-yl) amide **31** (35%, 39% ee) and the *N*-(cyclohex-1-en-1-yl) amide **32** (31%) (*Scheme 6*). The aziridines **33** and **35**, in turn, rearranged to **34** (69%, 75% ee) and **36** (72%, 43% ee), respectively, both derived from intramolecular carbene insertion. The α configuration of the sulfonamide group in **34** was deduced from NOESY experiments that indicated interactions between the protons at the functionalized (C(1)) and the bridgehead positions on the β-side. The absolute configuration of **36** was determined to be (*R*) by comparison of its optical rotation and HPLC retention time with those of an independently prepared sample of (*R*)-**36**. The reference compound (*R*)-**36** was synthesized *via* bromination of trinorbornene followed by carbonylation [36][37] to give **37**. Racemic **37** was partially resolved by recrystallization of its salt with (+)-(*R*)-α-methylbenzylamine and converted to the amine (*R*)-**38** *via Curtius* degradation with diphenylphosphoryl azide [38]. The optical rotation of (*R*)-**38** established an ee of 53% ee, based on the ϕ_D^{25} (*S*)-**38** [39] (see *Exper. Part*).

To our knowledge, these are the first base-induced rearrangements of sulfonylated aziridines to allylic amides ever reported. The reaction appears to be analogous to the corresponding rearrangement of epoxides [4][5], yields and enantioselectivities being

Scheme 6



in the same range. Further experiments to establish scope and limitations of this reaction are in progress in our laboratory.

Discussion. – The aziridine openings reported here involve enantioselective attack of a chiral nucleophile at one of two enantiotopic centers. This concept differs, at first glance, from that usually applied to desymmetrization of epoxides and aziridines based on chiral electrophilic catalysts and achiral reagents, and bears more resemblance to the Cu-catalyzed enantioselective addition reactions of *Grignard* [40] or dialkylzinc reagents to enones [41] or vinyloxiranes [42]. However, there is substantial experimental evidence that the catalyzed epoxide openings exhibit second-order kinetics with respect to catalyst concentration, which indicates a bimetallic mechanism for catalysis [43]. This suggests coordination of the nucleophile to the chiral catalyst prior to nucleophilic attack. These observations are supported by density-functional theory calculations that show coordination of the leaving group with the organometallic reagent in nucleophilic displacements with lithium organocuprates [44]. These observations should also apply to aziridine openings. Thus, in the electrophilic catalysis for epoxide opening, the nucleophile is delivered from a chiral catalyst, and in the

nucleophilic catalysis of aziridine opening, the N-atom of the aziridine may be coordinated to an electrophile, so that the mechanisms involved in these reactions are probably not fundamentally different.

This work was supported by the *Swiss National Science Foundation* (Grant Nos. 20-52581.97 and 2027-048156), by the *European Commission for Science, Research, and Development* (COST Action D12), the *Société Académique de Genève* (Fonds *Marc Birkigt*), and the University of Geneva. The authors are indebted to Mrs. *A. Pinto* and *J.-P. Saulnier* for the NMR spectra, and to Ms. *D. Klink* for the mass spectra.

Experimental Part

General. All reactions were carried out under N_2 by standard *Schlenk* techniques [45]. CH_2Cl_2 and MeCN were dried over CaH_2 and distilled. Et_2O, THF, and toluene were dried over Na/benzophenone and distilled. The other solvents were purchased from *Fluka* or *Merck* and used without purification. (−)-Sparteine · H_2SO_4 · 5 H_2O (*Fluka*) was extracted with base, and the free amine was distilled and stored under Ar at −78°. Flash chromatography (FC) [46]: silica gel *60 Merck 9385*. TLC: *Macherey-Nagel Polygram Sil G/UV*$_{254}$; detection by UV light or with phosphomolybdic acid.

The enantiomer excess of the products was determined by GC (*Lipodex E* and *γ-Dex* columns) or by HPLC (*Chiracel OD H*; *Chiracel OB H*; *Chiracel AD*; *Chiracel AS*, or *Chiracel OJ* columns); t_R in min. Optical rotations: *Perkin-Elmer 241* polarimeter; 10-cm quartz cells. IR Spectra: *Mattson Instruments Polaris* FT-IR instrument, NaCl cells, in cm^{-1}. NMR Spectra: *Varian-XL-200* (^1H at 200 MHz, ^{13}C at 50 MHz); *Bruker AMX-400* (^1H at 400 MHz, ^{13}C at 100 MHz), and *Bruker AMX-500* (^1H at 500, ^{13}C at 125 MHz), chemical shifts δ in ppm with respect to $SiMe_4$ (= 0 ppm), coupling constants in Hz. MS: *Varian CH4* or *SM1* spectrometer with electron impact or electrospray; *m/z* (rel. %). High-resolution (HR) MS: *VG-7070* analytical spectrometer (data system *11 250*, resolution 7000).

Aziridines. The aziridines were synthesized by Cu-catalyzed aziridination of the appropriate olefins with TsN=IPh [47] as described in the literature. For anal. data of **1**, **28**, and **35**, see [48], for **24**, see [49], for **26**, see [50], for **33**, see [51].

Catalysts and/or Ligands. The following catalysts and ligands were synthesized according to literature procedures: **4** [41b], **5** [52], **6** [53], **7** [54], **8** [55], **9a** [56] (free ligand), **9b** [57][58], **10** [59] (free ligand), **11** and **12**: [41c], **13** [22], and **14** [60] (free ligand).

The catalysts **9a**, **10**, and **14** were prepared by reaction of the free ligands with [$CuCl_2$] in MeOH [54].

{[2,2′-{[(1S,2S)-Cyclohexane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2−)}copper (**9a**): $[\alpha]_{578}^{20} = -351$ ($c = 0.008$, $CHCl_3$). MS (electrospray): 384.2 (M^+).

*{[2,2′-{[(1S,2S)-Cyclohexane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-di(*tert*-butyl)phenolato-κO]}(2−)}copper* (**9b**): $[\alpha]_{578}^{20} = -260$ ($c = 0.01$, $CHCl_3$). MS (electrospray): 608.6 (M^+).

{[2,2′-{[(1S,2S′)-1,2-Diphenylethane-1,2-diyl]bis[(nitrilo-κN]methylidyne]}bis[phenolato-κO]}(2−)}copper (**10**): $[\alpha]_{578}^{20} = +212.5$ ($c = 0.016$, $CHCl_3$). MS (electrospray): 482.14 (M^+).

*{2,2′[(1S)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-di(*tert*-butyl)phenolato-κO](2−)}copper* (**14**): $[\alpha]_{578}^{21} = -228.5$ ($c = 0.028$ ($CHCl_3$). MS: 778.6 (M^+).

[(R)-(1,1′-Binaphthalene-2,2′-diyl] 1-[(4S)-4,5-Dihydro-4-isopropyloxazol-2-yl]-1-methylethyl Phosphite (= *(4S)-2-{1-[[(11bR)-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxophosphepin-5-yl]oxy}-1-methylethyl]-4,5-dihydro-4-isopropyloxazole;* **16**). *(4S)-4,5-Dihydro-4-isopropyl-9α-dimethyloxazole-2-methanol* (**19**). For 28 h, 2-hydroxy-2-methylpropanoic acid (3.0 g, 29 mmol) and L-valinol (3.0 g, 29 mmol) were heated to reflux in *p*-xylene (90 ml), and H_2O was separated by means of a *Dean-Stark* trap. After evaporation, the residue was purified by FC (pentane/AcOEt 1:1): **19** (1.10 g, 22%). Pale yellow oil. $[\alpha]_D^{21} = -100.5$ ($c = 0.50$, $CHCl_3$). IR: 3390*m*, 1661*s*, 1559*m*, 1299*m*, 1180*w*, 990*m*, 868*m*, 789*m*. ^1H-NMR (400 MHz, $CDCl_3$): 0.88 (*d*, $J = 7.3$, 6 H); 0.95 (*d*, $J = 6.8$, 6 H); 1.44 (*s*, 6 H); 1.73–1.82 (*m*, 1 H); 3.64 (br. *s*, 1 H); 3.95 (*ddd*, $J = 9.6$, 7.6, 5.8, 1 H); 4.10 (*dd*, $J = 7.6$, 7.6, 1 H); 4.33 (*dd*, $J = 9.6$, 8.3, 1 H). ^{13}C-NMR (100 MHz): 17.7 (*q*); 18.4 (*q*); 27.7 (*q*); 27.9 (*q*); 32.3 (*d*); 713 (*t*); 134.6 (*s*); 172.3 (*s*).

Cyclic Phosphite **16**. (1*R*)-[1,1′-binaphthalene]-2,2′-diol (1.0 g, 3.5 mmol) in toluene (20 ml) was added at −78° to PCl_3 (0.30 ml, 3.5 mmol) and Et_3N (1.0 ml, 7 mmol). After stirring at r.t. for 24 h, the precipitate (Et_3NHCl) was filtered off, and the filtrate was added to Et_3N (2.6 g, 25.7 mmol) in toluene (20 ml) at −78°. After stirring for 5 min at −78°, **19** (0.60 g, 3.2 mmol) in toluene (5.0 ml) was added to the *in situ* prepared **18** [23]. The temp. was raised to 25° and the mixture stirred for 12 h. The soln. was filtered, the filtrate evaporated,

and the residue purified by FC (silica gel, petroleum ether/AcOEt 7:1): **16** (355 mg, 24%). Amorphous solid. $[\alpha]_D^{23} = -278$ ($c = 3.0$, $CHCl_3$). IR ($CHCl_3$): 3618*w*, 3020*s*, 2399*m*, 1522*s*, 1420*w*, 1222*s*, 1045*s*, 928*s*, 799*s*, 708*s*, 672*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*d*, $J = 7$, 3 H); 1.00 (*d*, $J = 6.7$, 3 H); 1.67 (*s*, 3 H); 1.74 (*s*, 3 H); 1.78–1.88 (*m*, 1 H); 4.02 (*ddd*, $J = 9.5, 7.5, 6.3$, 1 H); 4.12 (*dd*, $J = 6.8, 1.3$, 1 H); 4.35 (*dd*, $J = 8.2, 1.2$, 1 H); 7.20–7.27 (*m*, 2 H); 7.36–7.44 (*m*, 6 H); 7.49 (*d*, $J = 8.8$, 1 H); 7.86–7.92 (*m*, 2 H); 7.94 (*d*, $J = 8.8$, 1 H). ^{13}C-NMR (125 MHz): 17.9 (*q*); 18.7 (*q*); 28.0 (*d*, $J = 6.6$, *q*); 32.5 (*d*); 70.8 (*t*); 72.1 (*d*), 75.6 (*d*, $J = 10.7$, *s*); 121.9 (*d*); 122.4 (*d*); 123.0 (*d*, $J = 2.5$, *s*); 124.3 (*d*, $J = 5$, *s*); 124.6 (*d*); 124.8 (*d*); 125.8 (*d*); 126.0 (*d*); 126.9 (*d*); 127.0 (*d*); 128.1 (*d*); 128.2 (*d*); 129.3 (*d*); 130.0 (*d*); 131.1 (*s*); 131.4 (*s*); 132.6 (*s*); 132.7 (*d*, $J = 1.7$, *s*); 147.8 (*d*, $J = 2.5$, *s*); 147.9 (*d*, $J = 4.1$, *d*); 168.1 (*s*). ^{31}P-NMR (202 MHz, $CDCl_3$): 152.9. MS: 487 (5), 486 (25), 485 (75, M^+), 374 (34), 349 (10), 333 (25), 332 (100), 331 (42), 330 (25), 269 (11), 268 (80), 267 (12), 239 (20), 154 (40), 69 (22). HR-MS: 485.1765 ($C_{29}H_{28}NO_4P^{+\bullet}$; calc. 485.1756).

(+)-(9S)-9,9′-Biphenanthrene-10,10′-diyl Diisopropylphosphoramidite (*=(15bS)-*N,N*-Diisopropyldiphenanthro[9,10-*d*:9′,10′-*f*][1,3,2]dioxaphosphepin-4-amine*; **17**). Diisopropylphosphoramidous dichloride [27] (**21**; 79 mg, 0.39 mmol) was added, at $-40°$, to (−)-(9*S*)-9,9′-biphenanthrene-10,10′-diol ((*S*)-**20**) (150 mg, 0.39 mmol) and Et_3N (0.11 ml, 0.78 mmol) in toluene (10 ml). The mixture was stirred for 2.5 h at r.t. The solvent was evaporated, and the residue was purified by FC (silica gel, petroleum ether/AcOEt 3:1): **17** (113 mg, 57%). Colorless solid. M.p. 206–208°. $[\alpha]_D^{20} = +562.5$ ($c = 0.11$, $CHCl_3$). IR ($CHCl_3$): 3619*m*, 3458(br.), 3024*s*, 2399*m*, 1522*s*, 1391*m*, 1205*s*, 1045*s*, 928*m*, 799*s*, 666*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12–1.23 (*m*, 12 H); 3.26–3.52 (*m*, 2 H); 7.21–7.48 (*m*, 4 H); 7.51–7.63 (*m*, 2 H); 7.65–7.83 (*m*, 4 H); 8.42 (*dd*, $J = 7.6$, 1.7, 2 H); 8.53 (*dd*, $J = 7.8$, 1.0, 4 H). ^{13}C-NMR (50 MHz): 22.3 (*q*); 22.6 (*q*); 45.1 (*d*); 45.2 (*d*); 119.0 (*s*); 120.9 (*s*), 122.5 (*d*); 122.7 (*d*); 122.8 (*d*); 122.9 (*d*); 124.3 (*d*); 124.9 (*d*); 125.2 (*d*); 126.1 (*d*); 126.18 (*d*); 126.21 (*d*); 126.5 (*d*); 127.1 (*d*); 127.3 (*d*); 127.4 (*d*); 127.5 (*s*); 127.6 (*d*); 127.8 (*s*); 127.9 (*s*); 128.0 (*d*); 128.3 (*s*); 131.3 (*s*); 131.5 (*s*), 131.7 (*s*); 146.5 (*s*); 147.2 (*s*); 147.3 (*s*). ^{31}P-NMR (162 MHz, $CDCl_3$): 155.5. MS: 517 (8), 516 (16), 515 (96, M^+), 501 (31), 500 (37), 472 (23), 459 (18), 457 (51), 417 (16), 416 (65), 415 (86), 376 (10), 369 (32), 368 (100), 353 (23), 352 (62), 339 (28), 88 (15), 86 (15), 46 (77). HR-MS: 515.2003 ($C_{34}H_{30}NO_2P^{+\bullet}$; calc. 515.2014). Anal. calc. for $C_{34}H_{30}NO_2P$: C 79.26, H 5.86, N 2.71; found: C 79.26, H 6.12, N 2.51.

Cu-Catalyzed Opening of **1** *with* Grignard *Reagents: General Procedures. Method A*. To the appropriate Cu complex (0.04 mmol) and **1** (0.4 mmol) in THF (2.0 ml), the *Grignard* reagent (0.48 mmol) in Et_2O (0.5 ml) was added dropwise at 0°. After the addition, the mixture was stirred at 0° for the time indicated and then hydrolyzed with sat. NH_4Cl soln. (10 ml) and extracted with Et_2O (3×10 ml). The extract was washed with sat. NaCl soln. (10 ml), dried ($MgSO_4$), and evaporated, and the products were purified by FC.

Method B. A soln. of $[Cu(OTf)_2]$ (14.4 mg, 0.04 mmol) and the appropriate ligand were stirred in THF (2.0 ml) for 1 h at r.t. After addition of **1** (100 mg, 0.40 mmol), the mixture was cooled to 0°, and the *Grignard* reagent (0.40 mmol) in Et_2O (0.12 ml) was added dropwise. The mixture was stirred at 0° for the time indicated and then hydrolyzed with sat. NH_4Cl soln. The aq. layer was extracted with Et_2O (10 ml), the combined org. layer washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated, and the crude product purified by FC.

N-*(*trans-*2-Azidocyclohexyl)-4-methylbenzenesulfonamide* (**2a**) [19]: M.p. 69–71°. IR ($CHCl_3$): 3310*s*, 2965v*s*, 2469*w*, 2016v*s*, 1469*s*. ^{1}H-NMR (400 $CDCl_3$): 1.21–1.26 (*m*, 3 H); 1.60–1.72 (*m*, 2 H); 2.01–2.09 (*m*, 2 H); 2.43 (*s*, 3 H); 2.92–2.94 (*m*, 1 H); 3.04–3.09 (*m*, 2 H); 4.75 (*m*, $J = 5.9$, 1 H); 7.31 (*d*, $J = 8$, 2 H); 7.79 (*d*, $J = 8$, 2 H). ^{13}C-NMR (100 MHz): 21.5 (*q*); 23.7 (*t*); 30.1 (*t*); 30.8 (*t*); 32.5 (*t*); 56.7 (*d*); 63.6 (*d*); 127.1 (*d*); 129.6 (*d*); 137.5 (*s*); 143.5 (*s*). MS: 249 (1), 210 (19), 155 (38), 111 (38), 94 (22), 92 (14), 91 (100), 84 (17), 65 (22), 56 (38).

N-*(*trans-*2-Chlorocyclohexyl)-4-methylbenzenesulfonamide* (**2b**): M.p. 100–102° ([61]: 100–102°). IR ($CHCl_3$): 3378*w*, 3024*s*, 2945*w*, 1599*w*, 1450*w*, 1413*w*, 1335*m*, 1101*s*, 765*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.15–1.39 (*m*, 4 H); 1.51–1.81 (*m*, 4 H); 2.10–2.38 (*m*, 2 H); 2.42 (*s*, 3 H); 2.99–3.18 (*m*, 1 H); 3.61–3.81 (*m*, 1 H); 4.82 (*d*, $J = 5.3$, 1 H); 7.76 (*d*, $J = 8.2$, 2 H); 7.31 (*d*, $J = 8.2$, 2 H). ^{13}C-NMR (100 MHz): 33.5 (*t*); 35.5 (*t*); 38.6 (*t*); 62.3 (*d*); 64.5 (*d*); 127.7 (*d*); 129.2 (*d*); 138.1 (*s*); 143.9 (*s*). MS: 289 (11, M^+), 287 (31, M^+), 252 (14), 211 (12), 210 (100), 155 (77), 132 (21), 96 (15), 91 (98), 65 (19).

N-*(*trans-*2-Bromocyclohexyl)-4-methylbenzenesulfonamide* (**2c**): Colorless crystals. M.p. 104–106° ([21]: 105–107°). IR ($CHCl_3$): 3378*w*, 3024*s*, 2943*s*, 1599*w*, 1332*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.19–1.33 (*m*, 3 H); 1.36–1.40 (*m*, 1 H); 1.69–1.72 (*m*, 1 H); 1.92–2.01 (*m*, 1 H); 2.27–2.39 (*m*, 2 H); 2.43 (*s*, 3 H); 3.21–3.26 (*m*, 1 H); 3.94–3.99 (*m*, 1 H); 4.78 (*d*, $J = 5.6$, 1 H); 7.32 (*d*, $J = 8$, 2 H); 7.79 (*d*, $J = 8$, 2 H). ^{13}C-NMR (100 MHz): 33.4 (*t*); 34.9 (*d*); 38.1 (*t*); 59.3 (*d*); 63.5 (*d*); 127.5 (*d*); 129.6 (*d*); 137.1 (*s*); 143.6 (*s*). MS: 333 (23, M^+), 252 (16), 210 (97), 155 (82), 96 (62), 91 (100), 69 (21).

*4-Methyl-*N-*(*trans-*2-methylcyclohexyl)benzenesulfonamide* (**3a**): Colorless solid. M.p. 98–100°. IR ($CHCl_3$): 2929v*s*, 2857*s*, 1448*w*, 1415*w*, 1328*s*, 1157*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*d*, $J = 6.8$, 3 H);

1.08–1.25 (*m*, 5 H); 1.57–1.58 (*m*, 2 H); 1.70–1.72 (*m*, 2 H); 2.41 (*s*, 3 H); 2.64–2.65 (*m*, 1 H); 4.70–4.80 (*m*, 1 H); 7.27 (*d*, *J* = 8, 2 H); 7.76 (*d*, *J* = 8, 2 H). ^{13}C-NMR (100 MHz): 19.1 (*q*); 21.5 (*q*); 25.3 (*t*); 34.5 (*t*); 38.3 (*d*); 59.1 (*d*); 60.3 (*s*); 126.9 (*d*); 129.5 (*d*); 138.7 (*s*); 142.9 (*s*). MS: 267 (66, M^+), 210 (100), 155 (94), 91 (95), 65 (20). HR-MS: 267.1280 ($C_{14}H_{21}NO_2S^{+\bullet}$; calc. 267.12930). Anal. calc. for $C_{14}H_{21}NO_2S$: C 62.87, H 7.92, N 5.27; found: C 62.70, H 7.86, N 5.27.

Enantiomer separation of **3a**: HPLC (*Chiracel OD H*, hexane/^{i}PrOH 9 : 1, 0.5 ml/min): t_R 13.4 ((1*S*,2*S*)-**3a**), 14.5 ((1*R*,2*R*)-**3a**).

Absolute Configuration of **3a**. To the sulfonamide **3a** (100 mg, 1.50 mmol; obtained from **1** and MeMgBr in the presence of catalyst **8**) in liq. NH_3 (20 ml), Na (172 mg, 7.50 mmol) was added in small portions at −78°. The mixture was stirred at −78° for 2 h, whereupon an excess of NH_4Cl was added until the blue color disappeared. The solvent was evaporated slowly. The residue was dissolved in AcOEt (25 ml) and 2M HCl (25 ml). The aq. layer was washed with AcOEt (2 × 25 ml), then made basic with NH_4OH, and extracted with AcOEt (3 × 25 ml). The org. phase was dried (Na_2SO_4) and evaporated. The crude product was dissolved in Et_2O (20 ml) and precipitated with HCl gas. The precipitate was filtered, dissolved in 1M NaOH, and extracted with Et_2O to afford *trans*-2-methylcyclohexanamine (**22**) (104 mg, 61%). Transparent oil. $[\alpha]_D^{20} = +20.2$ ($c = 10.0$, Et_2O) for 55% ee ([62]: $[\alpha]_D^{19} = +30.8$ for (1*S*,2*S*)-**22**). B.p. 140–142°. IR ($CHCl_3$): 2927*s*, 2871*m*, 2361*w*, 1748*s*, 1597*w*, 1575*w*, 1456*m*, 1369*m*, 1257*s*, 1096*w*, 955*m*, 803*s*, 734*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.97 (*d*, *J* = 6.3, 3 H); 1.10–1.13 (*m*, 3 H); 1.55–1.80 (*m*, 4 H); 1.90–2.10 (*m*, 2 H); 2.28 (*dt*, *J* = 10.5, 4.5, 1 H); 3.60 (br. *s*, 2 H). ^{13}C-NMR (100 MHz): 19.1 (*q*); 25.8 (*t*); 26.2 (*t*); 34.2 (*t*); 36.3 (*t*); 40.8 (*d*); 56.7 (*d*).

4-Methyl-N-*(*trans-*2-pentylcyclohexyl)benzenesulfonamide* (**3b**): FC (pentane/AcOEt 15 : 1). Colorless solid. M.p. 55–58°. IR ($CHCl_3$): 3009*w*, 2930*s*, 2857*w*, 1448*w*, 1325*w*, 1221*s*, 1157*s*, 1091*w*, 799*s*, 769*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.2, 3 H); 0.84–1.82 (*m*, 17 H); 2.43 (*s*, 3 H); 2.85 (*ddd*, *J* = 10.1, 10.1, 4, 1 H); 4.29 (*d*, *J* = 8.9, 1 H); 7.30 (*d*, *J* = 8, 2 H); 7.83 (*d*, *J* = 8, 2 H). ^{13}C-NMR (125 MHz): 14.5 (*q*); 19.8 (*t*); 22.0 (*q*); 22.9 (*t*); 23.2 (*t*), 25.5 (*t*); 26.4 (*t*); 31.2 (*t*); 32.5 (*d*); 40.2 (*t*); 43.5 (*d*); 57.8 (*d*); 127.4 (*d*); 131.3 (*d*); 139.0 (*s*); 143.4 (*s*). MS: 323 (32, M^+), 280 (10), 266 (12), 210 (50), 172 (17), 168 (58), 155 (49), 152 (20), 96 (56), 95 (13), 92 (12), 91 (100), 82 (14), 69 (23), 67 (17), 65 (19), 56 (16), 55 (21). HR-MS: 323.1869 ($C_{18}H_{29}O_2NS^+$; calc. 323.1910).

Enantiomer separation of **3b**: HPLC (*ODH*, hexane/^{i}PrOH 9 : 1, 0.5 ml/min): t_R 10.0, 11.2.

N-*(*trans-*2-Isopropylcyclohexyl)-4-methylbenzenesulfonamide* (**3c**): FC (pentane/AcOEt 6 : 1). Colorless solid. M.p. 88–91°. IR ($CHCl_3$): 2937*m*, 2859*w*, 1599*w*, 1156*s*, 1092*w*, 766*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.46 (*d*, *J* = 6.7, 3 H); 0.76 (*d*, *J* = 6.7, 3 H); 0.85–1.22 (*m*, 4 H); 1.29–1.38 (*m*, 1 H); 1.48–1.60 (*m*, 2 H); 1.63–1.77 (*m*, 2 H); 1.96 (*dsept.*, *J* = 4.5, 2.8, 1 H); 2.35 (*s*, 3 H); 2.89–2.98 (*m*, 1 H); 4.19 (*d*, *J* = 8.9, 1 H); 7.21 (*d*, *J* = 8, 2 H); 7.69 (*d*, *J* = 8, 2 H). ^{13}C-NMR (125 MHz): 15.5 (*q*); 21.1 (*q*); 22.8 (*t*); 25.2 (*t*); 25.9 (*d*); 35.1 (*t*); 48.8 (*d*); 54.7 (*d*); 126.9 (*d*); 129.5 (*d*); 137.7 (*s*); 142.0 (*s*). MS: 295 (2, M^+), 155 (14), 140 (17), 124 (11), 96 (100), 91 (35), 69 (42), 65 (12), 55 (11). HR-MS: 295.1605 ($C_{16}H_{25}NO_2S^+$, calc. 295.1606).

Enantiomer separation of **3c**: HPLC (*ODH*, hexane/^{i}PrOH 9 : 1, 0.5 ml/min): t_R 15.3, 16.5.

4-Methyl-N-*(*trans-*2-phenylcyclohexyl)benzenesulfonamide* (**3d**). FC (hexane/AcOEt 9 : 1). Colorless crystals. M.p. 146–148°. $[\alpha]_D^{21} = -5.89$ ($c = 2.01$, $CHCl_3$) for 53% ee. IR ($CHCl_3$): 3027*m*, 2936*m*, 2859*w*, 1599*w*, 1493*w*, 1449*w*, 1405*w*, 1335*w*, 1228*m*, 1160*s*, 1093*w*, 1073*w*, 897*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20–1.45 (*m*, 5 H); 1.68–1.85 (*m*, 3 H); 2.33 (*ddd*, *J* = 11.3, 11.0, 3.4, 1 H); 2.42 (*s*, 3 H); 3.02–3.15 (*m*, 1 H); 4.18 (*d*, *J* = 4.4, 1 H); 6.84 (*d*, *J* = 6.9, 2 H); 7.0–7.18 (*m*, 5 H); 7.32 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (100 MHz): 21.5 (*q*); 25.0 (*t*); 25.8 (*t*); 34.7 (*t*); 35.0 (*t*); 50.4 (*d*); 57.4 (*d*); 126.8 (*d*); 127.0 (*d*); 128.8 (*d*); 129.4 (*d*); 136.9 (*s*); 142.1 (*s*); 142.7 (*s*). MS: 329 (3, M^+), 210 (14), 174 (55), 159 (14), 158 (100), 157 (17), 155 (27), 129 (11), 115 (13), 96 (14), 91 (90), 65 (14). HR-MS: 329.1418 ($C_{19}H_{23}NO_2S^{+\bullet}$; calc. 329.1449).

Enantiomer separation of **3d**: HPLC (*Chiracel AD*, hexane/^{i}PrOH 25 : 1, 0.5 ml/min): t_R 35.4 ((1*S*,2*R*)-**3d**), 42.3 ((1*R*,2*S*)-**3d**).

Absolute Configuration of **3d**. A soln. of TsCl (648 mg, 3.40 mmol) in CH_2Cl_2 (5.0 ml) was added dropwise to enantiomerically enriched (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexanamine (1*S*,2*R*-**23**) (53% ee; 585 mg, 3.36 mmol) [63] and Et_3N (0.94 ml, 6.7 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at r.t. for 2 h, whereupon H_2O (20 ml) was added. After extraction with CH_2Cl_2 (3 × 20 ml), the org. phase was washed with sat. NaCl soln. and dried ($MgSO_4$): 46% of (1*S*,2*R*)-**3d**. $[\alpha]_D^{20} = +12$ ($c = 1.84$, $CHCl_3$) for 53% ee.

4-Methyl-N-*[*trans-*2-(2,4,6-trimethylphenyl)cyclohexyl]benzenesulfonamide* (**3e**): FC (hexane/AcOEt 9 : 1). Colorless crystals. M.p. 143–146°. IR ($CHCl_3$): 3315*w*, 2938*m*, 2858*w*, 1450*w*, 1401*w*, 1317*w*, 1226*s*, 1212*m*, 1159*m*, 1093*w*, 1063*w*, 908*w*, 854*w*, 733*w*, 716*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.21–1.48 (*m*, 5 H); 1.60–1.88 (*m*, 6 H); 1.93 (*s*, 3 H); 2.24 (*s*, 3 H); 2.30 (*s*, 3 H); 2.44 (*s*, 3 H); 2.93 (*ddd*, *J* = 10.8, 10.8, 3.7, 1 H); 3.56–3.63 (*m*, 1 H); 4.09 (*s*, *J* = 4, 1 H); 6.54 (*s*, 1 H); 6.81 (*s*, 1 H); 7.16 (*d*, *J* = 8, 2 H); 7.41 (*d*, *J* = 8, 2 H). ^{13}C-NMR

(100 MHz): 19.3 (*t*); 20.6 (*q*); 20.9 (*q*); 21.4 (*q*); 21.9 (*q*); 22.7 (*t*); 24.9 (*t*); 26.4 (*t*); 29.8 (*t*); 35.5 (*t*); 45.5 (*d*); 54.6 (*d*); 126.9 (*d*); 129.2 (*d*); 129.5 (*d*); 131.6 (*d*); 133.8 (*s*); 135.9 (*s*); 136.0 (*s*); 136.9 (*s*); 137.3 (*s*); 142.7 (*s*). MS: 372 (11), 371 (43, M^+), 217 (16), 216 (100), 199 (14), 154 (14), 133 (59), 96 (22), 91 (37), 56 (15). HR-MS: 371.1938 ($C_{22}H_{29}NO_2S^{+\bullet}$; calc. 371.1919).

Enantiomer separation of **3e**: HPLC (Chiracel *OD H*, 0.5 ml/min): t_R 17.1, 24.8.

4-Methyl-N-*(*trans-*6-methylcyclohex-3-enyl)benzenesulfonamide* (**25**): FC (hexane/AcOEt 9:1). M.p. 79–881°. IR ($CHCl_3$): 3542*w*, 3382*m*, 3272*w*, 3028*s*, 2924*m*, 2837*w*, 2359*w*, 1599*m*, 1415*m*, 1227*s*, 1158*s*, 1094*m*, 953*w*, 814*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*d*, *J* = 6.4, 3 H); 1.65–1.90 (*m*, 3 H); 2.14–2.25 (*m*, 2 H); 2.48 (*s*, 3 H); 3.11–3.20 (*m*, 1 H); 4.64 (*d*, *J* = 8.8, 1 H); 5.40–5.48 (*m*, 1 H); 5.54–5.61 (*m*, 1 H); 7.29 (*d*, *J* = 8.4, 2 H); 7.76 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (100 MHz): 18.3 (*q*); 21.5 (*q*); 31.8 (*t*); 32.9 (*d*); 54.4 (*d*); 123.8 (*d*); 126.3 (*d*); 127.0 (*d*); 129.6 (*d*); 138.6 (*s*); 143.1 (*s*). MS: 265 (6, M^+), 213 (6), 212 (12), 211 (100), 155 (45), 147 (22), 139 (87), 120 (15), 110 (12), 94 (86), 92 (13), 91 (95), 79 (12), 67 (12), 65 (20), 56 (36), 55 (10). HR-MS: 265.1178 ($C_{14}H_{19}NOS^{+\bullet}$; calc. 265.1136).

Enantiomer separation of **25**: HPLC (*Chiracel OD H*, hexane/^{i}PrOH 9:1, 0.5 ml/min): t_R 14.1, 16.0.

4-Methyl-N-*(*trans-*2-methylcyclopentyl)benzenesulfonamide* (**27**): FC (hexane/AcOEt 9:1). Colorless oil. IR ($CHCl_3$): 2960*w*, 2872*w*, 1457*w*, 1418*w*, 1328*m*, 1158*s*, 1093*m*, 910*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*d*, *J* = 6.4, 3 H); 1.05–1.15 (*m*, 1 H); 1.20–1.30 (*m*, 1 H); 1.45–1.70 (*m*, 4 H); 1.75–1.90 (*m*, 1 H); 2.43 (*s*, 3 H); 3.00–3.10 (*m*, 1 H); 4.39 (*d*, *J* = 7.9, 1 H); 7.30 (*d*, *J* = 8, 2 H); 7.76 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR (100 MHz): 17.6 (*q*); 21.4 (*q*); 21.6 (*t*); 31.6 (*t*); 32.9 (*t*); 41.2 (*d*); 61.7 (*d*); 127.1 (*d*); 129.6 (*d*); 135.0 (*d*); 138.1 (*d*); 143.1 (*s*); 143.2 (*s*). MS: 253 (45, M^+), 224 (15), 211 (13), 210 (98), 155 (71), 98 (50), 92 (17), 91 (100), 82 (24), 65 (24), 56 (12), 55 (15). HR-MS: 253.1139 ($C_{13}H_{19}NOS^{+\bullet}$; calc. 253.1136).

Enantiomer separation of **27**: HPLC (*Chiracel OB,H*, hexane/^{i}PrOH 9:1, 0.4 ml/min): t_R 26.4, 29.4.

Rearrangement of Aziridines to Allylic Amines. General Procedure. (–)-Sparteine (340 mg, 1.45 mmol) in Et_2O (1.0 ml) was added within 10 min at –78° to ^{s}BuLi in Et_2O (3.0 ml). After stirring for 1 h at –78°, the aziridine (0.50 mmol) was added, and the mixture was stirred for 4 h at –78°. It was warmed to r.t., and sat. NH_4Cl soln. was added. The mixture was extracted with Et_2O (3 × 10 ml), the org. layer dried (Na_2SO_4) and evaporated, and the crude product purified by FC.

Rearrangement of **1**. FC (pentane/AcOEt 4:1) gave *N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (**31**; 35%) and *N*-(cyclohex-1-en-1-yl)-4-methylbenzenesulfonamide (**32**; 31%).

Data of **31** [64]: Colorless solid. M.p. 104–106° ([65]: 108–109°). $[\alpha]_D^{21} = +19.8$ (*c* = 1.50, $CHCl_3$) for 39% ee. IR ($CHCl_3$): 3541*w*, 3389*m*, 3272*w*, 3024*s*, 2926*m*, 2817*w*, 2364*w*, 1599*m*, 1411*m*, 1231*s*, 1157*s*, 1094*m*, 978*w*, 811*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.49–1.69 (*m*, 3 H); 1.71–1.79 (*m*, 1 H); 1.82–2.01 (*m*, 2 H); 2.43 (*s*, 3 H); 3.78–3.85 (*m*, 1 H); 4.58 (*d*, *J* = 8.5, 1 H); 5.32–5.38 (*m*, 1 H); 5.74–5.79 (*m*, 1 H); 7.31 (*d*, *J* = 8.2, 2 H); 7.78 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR (125 MHz): 19.2 (*t*); 21.5 (*q*); 24.4 (*t*); 30.2 (*t*); 48.9 (*d*); 126.9 (*d*); 127.0 (*d*); 129.6 (*d*); 131.5 (*d*); 138.3 (*s*); 143.2 (*s*).

Enantiomer separation of **31**. HPLC (*Chiracel AS*, hexane/^{i}PrOH 9:1, 0.5 ml/min): t_R 26, 29.

Data of **32** [65]: Semi-solid. IR ($CHCl_3$): 3555*w*, 3361*m*, 3282*w*, 3017*s*, 2847*w*, 2361*w*, 1603*m*, 1413*m*, 1214*s*, 1163*s*, 1084*m*, 943*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.22–1.31 (*m*, 2 H); 1.42–1.58 (*m*, 2 H); 1.62–1.81 (*m*, 2 H); 1.87–1.93 (*m*, 1 H); 2.11–2.18 (*m*, 1 H); 2.46 (*s*, 3 H); 4.22–4.27 (*m*, 1 H); 4.54 (*d*, *J* = 4.5, 1 H); 7.33 (*d*, *J* = 7.8, 2 H); 7.69 (*d*, *J* = 7.8, 2 H). ^{13}C-NMR (125 MHz): 20.4 (*q*); 21.5 (*q*); 24.9 (*t*); 27.2 (*t*); 32.7 (*t*); 50.0 (*d*); 127.1 (*d*); 129.6 (*d*); 131.7 (*s*); 143.7 (*s*).

4-Methyl-N-*[*rel-*(1*R*,*3a*S*,*6a*S*)-octahydropentalen-1-yl]benzenesulfonamide* (**34**). FC (SiO_2, pentane/AcOEt 4:1). Yield 71%. Colorless solid. M.p. 106–108°. $[\alpha]_D^{21} = +29.1$ (*c* = 0.975, $CHCl_3$) for 75% ee. IR ($CHCl_3$): 3385*w*, 3021*s*, 2951*s*, 2361*w*, 1600*w*, 1452*w*, 1341*m*, 1156*s*, 1092*s*, 926*w*, 761*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.00–1.11 (*m*, 1 H); 1.12–1.39 (*m*, 4 H); 1.42–1.71 (*m*, 4 H); 1.82–1.93 (*m*, 1 H); 2.29–2.38 (*m*, 2 H); 2.45 (*s*, 3 H); 3.51–3.62 (*m*, 1 H); 4.62 (*d*, *J* = 7.4 (1 H); 7.32 (*d*, *J* = 8.3, 2 H); 7.79 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR (125 MHz): 21.4 (*q*); 27.2 (*t*); 27.9 (*t*); 29.3 (*t*); 30.5 (*t*); 35.4 (*t*); 41.2 (*d*); 45.4 (*d*); 57.0 (*d*); 127.0 (*d*); 129.5 (*d*); 137.9 (*s*). MS: 279 (23, M^+), 250 (15), 211 (13), 210 (100), 184 (17), 155 (62), 124 (68), 108 (21), 107 (15), 92 (16), 91 (88), 79 (15), 67 (14), 65 (19), 56 (15), 55 (18). HR-MS: 279.1287 ($C_{15}H_{21}O_2NS^{+\bullet}$; calc. 279.1293).

Enantiomer separation of **34**: HPLC (*Chiracel OD H*, hexane/^{i}PrOH 25:1, 0.5 ml/min): t_R 27, 29.

4-Methyl-N-*(tricyclo[2.2.1.0^{2,6}]hept-3-yl)benzenesulfonamide* (**36**). Reaction in pentane. FC (pentane/AcOEt 4:1). Yield 72%. Colorless solid. M.p. 121–122°. $[\alpha]_D^{21} = -0.7$ (*c* = 1.04, $CHCl_3$) for 43% ee. IR ($CHCl_3$): 3388*w*, 3035*w*, 2875*w*, 1600*w*, 1418*w*, 1339*m*, 1292*w*, 1231*s*, 1159*s*, 1987*m*, 910*w*, 813*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.85–0.90 (*m*, 1 H); 1.05–1.12 (*m*, 2 H); 1.16 (*d*, *J* = 10.7, 2 H); 1.26 (*d*, *J* = 10.7, 2 H); 1.49 (*t*, *J* = 10.7, 1 H); 1.76 (*s*, 1 H); 2.39 (*s*, 3 H); 3.18 (*d*, *J* = 7.25, 1 H); 4.73 (*d*, *J* = 2.25, 1 H); 7.27 (*d*, *J* = 7.8, 2 H); 7.75 (*d*, *J* = 7.8, 2 H). ^{13}C-NMR (125 MHz): 10.3 (*q*); 11.9 (*d*); 14.6 (*d*); 21.5 (*d*); 29.3 (*t*); 31.3 (*q*); 34.0 (*q*); 58.9

(*d*); 127.0 (*d*); 129.6 (*d*); 138.0 (*s*); 143.1 (*s*). MS: 263 (7, M^+), 108 (84), 106 (15), 93 (17), 92 (100), 91 (79), 81 (22), 80 (14), 79 (11), 77 (10), 67 (11), 65 (18). HR-MS: 263.0972 ($C_{14}H_{17}O_2NS^{+\bullet}$; calc. 263.0980).

Enantiomer separation of **36**: HPLC (*Chiracel OD H*, hexane/^{i}PrOH 9:1, 0.5 ml/min): t_R 15.3 ((*S*)-**36**), 16.3 (*R*)-**36**).

Absolute Configuration of **36**. *Partial Resolution of* **37**: (+)-(*R*)-α-methylbenzylamine (1.66 g, 13.8 mmol) was added dropwise to racemic tricyclo[2.2.1.0^{2,6}]heptane-3-carboxylic acid (**37**) [36][37] (1.90 g, 13.8 mmol) in Et_2O (40 ml). A precipitate formed immediately. The mixture was stirred for 1.5 h and then evaporated. The recovered crude salt (3.44 g) was dissolved in refluxing acetone (30 ml), to which hot hexane (30 ml) was added slowly. The soln. was cooled, whereupon crystallization started. After 3 recrystallizations, 650 mg of salt was obtained having $[\alpha]_D^{21} = +24.3$ ($c = 0.82$, $CHCl_3$). The salt was dissolved in 20% HCl soln. (10 ml), to which solid NaCl (500 mg) was added. The soln. was extracted with AcOEt (5 × 20 ml), the org. layer washed (sat. NaCl soln.), dried, and evaporated to yield enantiomer-enriched acid (*R*)-**37** (323 mg, 17%). $[\alpha]_D^{21} = +12.3$ ($c = 2.0$, EtOH) for 53% ee, determined on (*R*)-**36**).

Curtius *Degradation of (*R*)-***37***. (3*R*)-Tricyclo[2.2.1.0^{2,6}]heptan-3-amine* ((*R*)-**38**). To the enantiomer-enriched (*R*)-**37** (prepared above; 300 mg, 2.21 mmol) in toluene (20 ml), Et_3N (1.21 ml) and diphenylphosphoryl azide (1.19 g) were added at 0°. The mixture was stirred for 40 min at r.t., and H_2O (10 ml) was added. The soln. was concentrated to *ca.* 50%, the aq. layer extracted with Et_2O (4 × 15 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the crude product purified by FC (pentane/AcOEt 9:1): carbonyl azide (190 mg, 54%). Yellowish oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.23–1.43 (*m*, 3 H); 1.36–1.45 (*m*, 3 H); 1.51–1.55 (*m*, 1 H); 2.24–2.27 (*m*, 1 H); 2.42–2.44 (*m*, 1 H). ^{13}C-NMR (125 MHz): 10.3 (*d*); 11.6 (*d*), 12.9 (*d*), 30.6 (*t*); 33.7 (*d*); 34.4 (*t*); 52.0 (*d*); 181.3 (*s*).

The azide (180 mg, 1.10 mmol) was refluxed in toluene (10 ml) for 30 min, whereupon 1M HCl (4.0 ml) was added. Refluxing was continued for 2 h. After cooling, 20% NaOH soln. was added until the pH of the soln. reached 12. The mixture was extracted with Et_2O (4 × 20 ml) and the extract washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated: free amine (*R*)-**38**. Colorless oil. $[\alpha]_D^{21} = +8.2$ ($c = 1.0$, EtOH) for 53% ee, determined on (*R*)-**36** ([39]: $[\alpha]_D^{25} = -67$ (neat for (*S*)-**38**)). IR ($CHCl_3$) 3334*w*, 2927*s*, 2361*w*, 1597*w*, 1575*w*, 1456*m*, 1369*m*, 1167*s*, 1096*w*, 955*m*, 814*s*, 734*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.97–1.02 (*m*, 1 H); 1.10–1.25 (*m*, 4 H); 1.26–1.31 (*m*, 1 H); 1.37 (*d*, $J = 10.4$, 1 H); 1.91 (*s*, 1 H); 3.48 (*m*, 3 H); 4.37 (br. *s*, 1 H). ^{13}C-NMR (125 MHz): 10.3 (*d*); 12.1 (*d*); 14.7 (*d*); 29.0 (*t*); 30.7 (*t*); 34.1 (*d*); 56.4 (*d*).

*Sulfonamidation of (*R*)-***38***.* A soln. of TsCl (130 mg, 0.68 mmol) in CH_2Cl_2 (2.0 ml) was added dropwise to (*R*)-**38** (70 mg, 0.57 mmol) and Et_3N (0.16 ml, 1.14 mmol) in CH_2Cl_2 (5.0 ml). After 2 h stirring at r.t., H_2O (10 ml) was added, and the mixture was extracted with sat. NaCl soln., dried ($MgSO_4$), and evaporated: (*R*)-**36** (93 mg, 62%). Colorless solid. $[\alpha]_D^{21} = -1.01$ ($c = 0.99$, $CHCl_3$) for 53% ee.

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Received October 12, 2000