Polish J. Chem., **77**, 867–879 (2003) **ORGANIC CHEMISTRY**

Synthesis of 3-Benzyl-1,3-thiazolidines by [2+3]-Cycloaddition of Sonochemically Generated Azomethine Ylides with Thiocarbonyl Compounds

by A. Gebert[1*], A. Linden[1], G. Mlostoń[2] and H. Heimgartner[1]**

[1]*Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*
[2]*Section of Heteroorganic Compounds, University of Łódź, Narutowicza 68, PL-90-136 Łódź, Poland*

(Received February 11th, 2003; revised manuscript March 18th, 2003)

Sonification of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (**5a**) in the presence of LiF led to the formation of the reactive azomethine ylide **1d**, which was intercepted by cyclic thioketones to give spirocyclic 1,3-thiazolidines. In the case of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**13**), the 1:1- and 1:2-cycloadduct, respectively, was formed as the major product depending on the ratio of the starting materials. With 1,3-thiazole-5(4*H*)-thiones, **1d** undergoes stereoselective [2+3]-cycloadditions with the C=S group to yield spirocyclic 1:1-adducts. In the case of the 1,3-dipole generated from *N*-benzyl-*N*-(methoxymethyl)-*N*-[1-(trimethylsilyl)ethyl]amine (**5b**), the [2+3]-cycloaddition proceeded in a non-regioselective manner leading to a mixture of regio- and diastereoisomers.

Key words: azomethine ylides, crystal structure, 1,3-dipolar cycloaddition, 1,3-thiazolidines, thiocarbonyl compounds

The suitability of azomethine ylides **1** as building blocks in the synthesis of five-membered nitrogen-heterocycles is well documented [1–3]. Many examples of their 1,3-dipolar cycloadditions with electron-poor alkenes and acetylenes, leading to pyrrolidine and pyrrol derivatives [1–6], are known, and these reactions have frequently been used in the total syntheses of alkaloids and other natural products, as well as in the synthesis of non-natural biologically active compounds. Recent examples are the syntheses of the alkaloids Epibatidine [7] and Epiboxidine [8], the carbapenem skeleton [9], and the preparation of a non-peptidic Thrombine inhibitor [10]. On the other hand, [2+3]-cycloadditions with heterodipolarophiles, such as carbonyl compounds, imines, ketenes, isocyanates, isothiocyanates, and thiocarbonyl compounds, which yield five-membered nitrogen-heterocycles with two heteroatoms, have been reported [1–3]. For example, a novel synthesis of the penam skeleton from azomethine ylides and C=S compounds has been published recently [11].

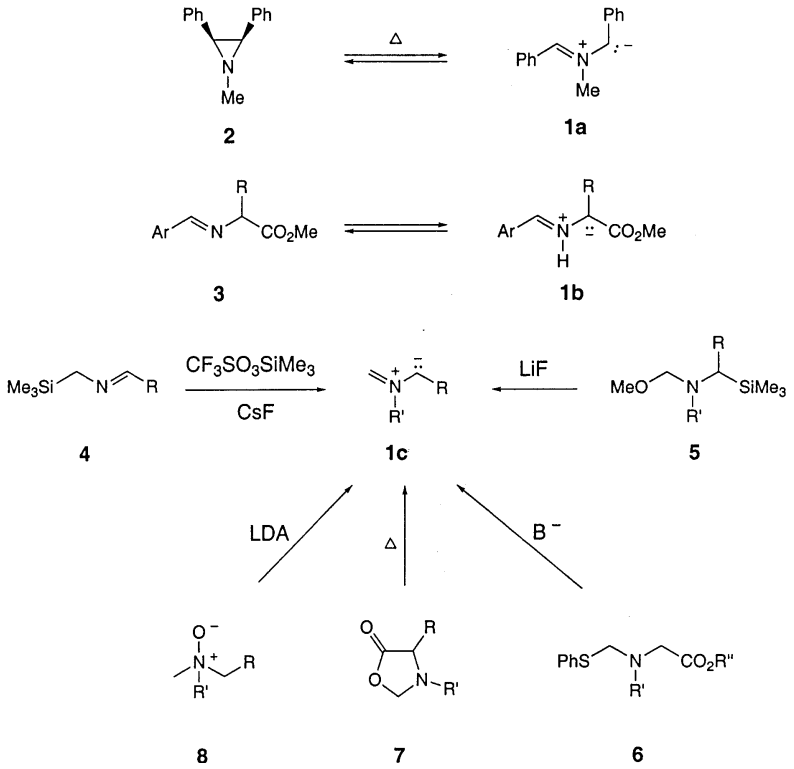
---

* Part of the PhD Thesis of *A.G.*, Universität Zürich, 2001; present address: *F. Hoffmann-La Roche AG*, Basel.

**Author for correspondence.

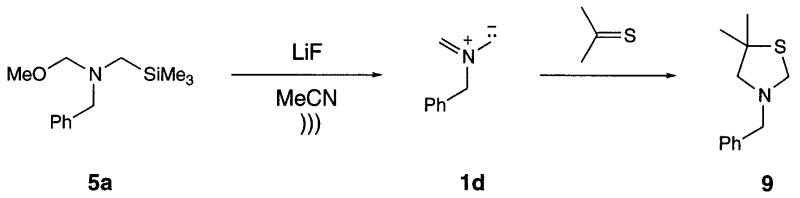
In general, azomethine ylides **1** are generated *in situ* as reactive intermediates in the presence of the appropriate dipolarophile. A couple of methods for their generation are shown in Scheme 1. In addition to the classical, stereoselective thermal ring opening of aziridines (**2** → **1a**) [12–15], azomethine ylides can be generated by a prototropic 1,2-H shift in imines of α-aminoesters (**3** → **1b**) [16], by desilylation methodology (**4** → **1c**) [17], (**5** → **1c**) [18], by 1,3-elimination of thiophenol from α-{[(phenylthio)methyl]amino}esters (**6** → **1c**) [19], by decarboxylation of 1,3-oxazolidin-5-ones (**7** → **1c**) [20,21], by dehydration of N-oxides (**8** → **1c**) [22], and by addition of carbenes or carbenoids to imines [23,24].

Scheme 1



In the last few years, we have studied extensively [2+3]-cycloadditions of azomethine ylides **1** with C=S groups as a convenient synthetic approach to 1,3-thiazolidines. In the described reactions, the azomethine ylides have been generated from aziridines [26–29], imines of α-aminoesters [30], and *N*-benzylidene(trimethylsilyl)methylamines [31,32], respectively. In the present paper, we report on [2+3]-cycloadditions of *N*-benzylazomethine ylide **1d** with thioketones and 1,3-thiazole-5(4*H*)-thiones leading to 3-benzyl-1,3-thiazolidines of type **9** (Scheme 2). The precursor of **1d** was *N*-benzyl-*N*-(methoxymethyl)[(trimethylsilyl)methyl]amine (**6a**); **1d** was generated *in situ* by sonification [33] in the presence of LiF [18].

Scheme 2



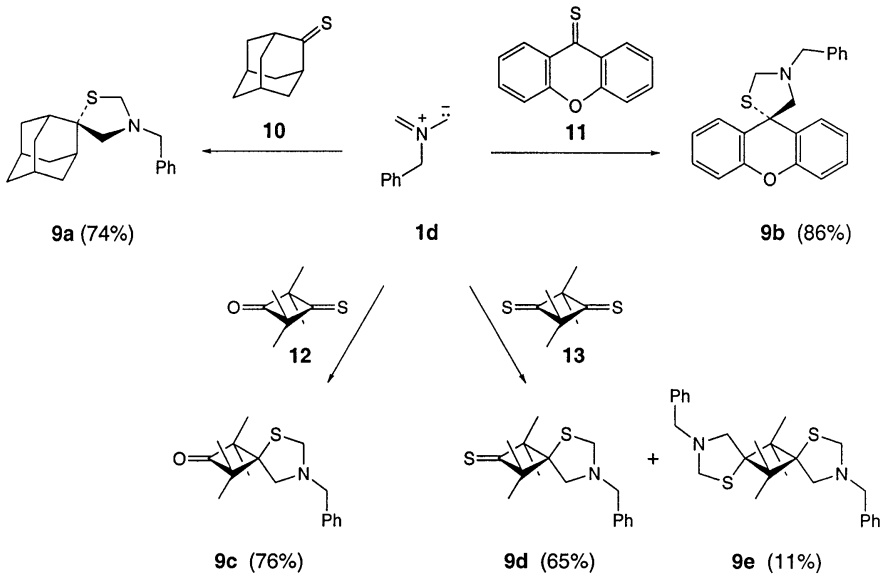
5a **1d** **9**

RESULTS AND DISCUSSION

To a solution of adamantanethione (**10**) and **6a** (ratio 1:2) in MeCN, LiF was added, and the mixture was treated with ultrasound (see ref. [33]) until no **10** could be detected by TLC. After cooling to room temperature, the mixture was filtered through Celite and the crude product was purified by chromatography. The cycloadduct **9a** was obtained in 74% yield (Scheme 3). Crystallization from i-PrOH/CH_2Cl_2 gave colorless crystals suitable for an X-ray crystal-structure determination. The structure of the spirocyclic molecule is shown in Figure 1.

Similar reactions were carried out with 9*H*-xanthene-9-thion (**11**), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**12**), and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**13**). In the cases of **11** and **12**, the 1:1-cycloadducts **9b** and **9c**, respectively,

Scheme 3



9a (74%) **1d** **9b** (86%)

9c (76%) **9d** (65%) **9e** (11%)

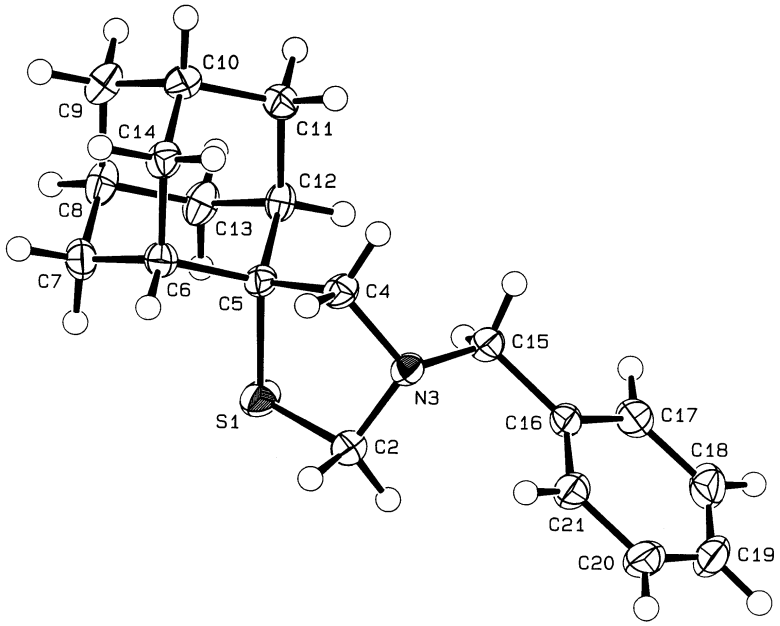
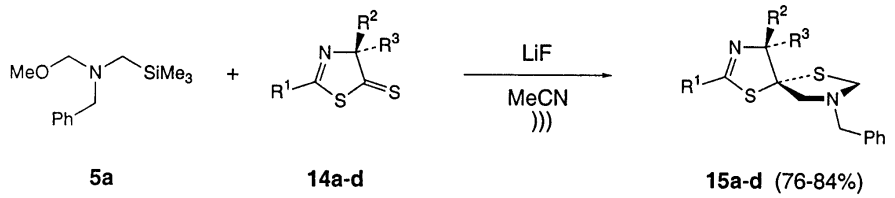


Figure 1. ORTEP plot [34] of the molecular structure of **9a** (arbitrary numbering of atoms; 50% probability ellipsoids).

were obtained in high yield (Scheme 3). No cycloadduct could be isolated in the reaction with 9*H*-fluorene-9-thione, which is known to be the most reactive dipolarophile. The only product formed under these conditions was bisfluorenylidene [30]. It is worth mentioning that only the monoadduct **9c** was formed with **12**, although an excess of **6a** was used, and Padwa and Dent had shown that **1d** is able to undergo a 1,3-dipolar cycloaddition with ketones [18]. On the other hand, dithione **13** reacted to give a mixture of monoadduct **9d** as the major product (65%) and a bisadduct **9e** as the minor one (11%). Treatment of a 1:4-mixture of **13** and **6a** under analogous conditions led to the bisadduct **9e** as the sole product in 67% yield. The structure of **9e** has been determined on the basis of its NMR spectra: all four methyl groups absorb as one singlet in the ^{1}H- (1.23 ppm) as well as in the ^{13}C-NMR spectrum (25.4 ppm). Therefore, the two 1,3-thiazolidine rings are in a *trans* relationship, as two different methyl signals are to be expected in the *cis*-isomer.

It has been shown that 1,3-thiazole-5(4*H*)-thiones **14** are also very efficient C=S dipolarophiles [26,31,35–37], *e.g.*, they react with azomethine ylides generated from aziridines [26] or *N*-benzylidene(trimethylsilyl)methylamine [31] to give spiroheterocyclic 1:1-adducts. Similarly, the reaction of **14a–d** with **5a** in the presence of LiF by sonification with ultrasound gave a single product in each case. Based on the spectroscopic data, structures **15a–d** (Scheme 4) were proposed and, in the case of **15d**, the structure was established by X-ray crystallography with single crystals grown from i-PrOH/MeOH (Figure 2). Both five-membered rings have an envelope conformation. The saturated ring has N(4) (numbering of the atoms according to Figure 2) as the envelope flap, while the spiro-C atom, C(2), acts as the envelope flap in the other ring.

Scheme 4



5a **14a-d** **15a-d** (76-84%)

a: R^1 = Ph, R^2 = R^3 = Me **b**: R^1 = Ph, R^2–R^3 = –$(CH_2)_4$–
c: R^1 = $PhCH_2$, R^2 = R^3 = Me **d**: R^1 = Ph, R^2 = Me, R^3 = $PhCH_2$

The reaction with the 4-benzyl-4-methyl derivative **14d** was performed with the pure (*R*)-enantiomer (*cf.* ref. [31]), and only one product with $[\alpha]_D$ = +40.7 (c = 1.6, $CHCl_3$) was obtained. Therefore, the [2+3]-cycloaddition to give **15d** occurred diastereoselectively *anti* to the benzyl residue, *i.e.*, from the sterically less hindered side. The absolute configuration of **15d** was confirmed by the diffraction experiment to be 4*R*,5*R*.

The analogous reaction of **14a**,**b** with the methyl-substituted **5b** proceeded non-regioselectively to give products of type **16** and **17** (Scheme 5). In the case of **14a**, the reaction was complete after 24 h. Chromatographic separation gave two frac-

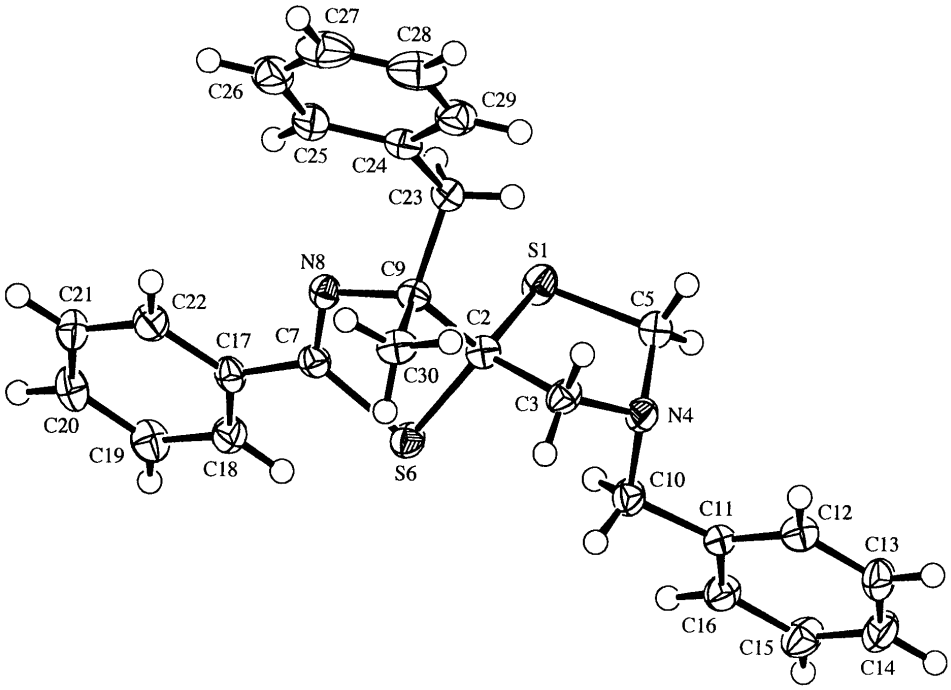
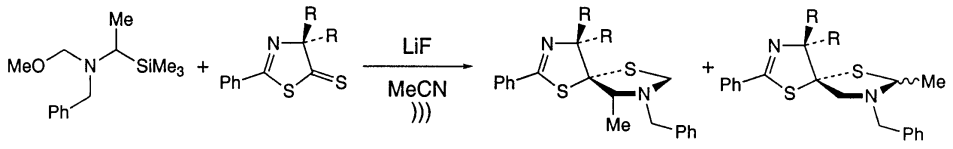


Figure 2. ORTEP plot [34] of the molecular structure of **15d** (arbitrary numbering of atoms; 50% probability ellipsoids).

Scheme 5



5b **14a,b** **16a,b** **17a,b**

a: R = Me **b**: R–R = $-(CH_2)_4-$

tions in a ratio of 1:2 in favor of the less polar one (total yield 59%). According to the NMR spectra, the more polar **16a** was a single diastereoisomer, whereas the less polar fraction **17a** consisted of a *ca.* 1:2-mixture of two diastereoisomers, as all signals were doubled. Similar results were obtained with **14b**: the more polar fraction was a single diastereoisomer, and the less polar one was a mixture of two diastereoisomers. Based on the chemical shifts in the ^{1}H-NMR spectra and on steric grounds, we propose that **16a**,**b** are the 4-methyl derivatives with the methyl group in a *trans* relationship with respect to the disubstituted C(9) and C(6), respectively. The mixtures of diastereoisomers **17a**,**b**, therefore, should bear the methyl group at C(2) of the 1,3-thiazolidine ring. All attempts to separate the diastereoisomers of **17a** and **17b** by chromatography, even with HPLC, failed.

Crystallization of **16b** from i-PrOH/$CHCl_3$ yielded single crystals suitable for an X-ray crystal-structure determination. The molecular structure shown in Figure 3 proved the assumption of the methyl group being at C(4) and *trans* to the quarternary C(9) (numbering of the atoms according to Figure 3). The 1,3-thiazole and the cyclopentane rings have envelope conformations with the flap of the envelope being C(5) and C(9), respectively. The 1,3-thiazolidine ring containing S(1) has a half-chair conformation twisted on N(3)–C(4).

In conclusion, it has been shown that the symmetrical *N*-benzyl azomethine ylide **1d**, which bears no substituent at C(1) and C(3), undergoes smooth [2+3]-cycloadditions with the C=S group of aliphatic, non-enolizable cyclic thioketones **10–13** and 1,3-thiazole-5(4*H*)-thiones **14** to give N-benzylated spirocyclic 1,3-thiazolidines **9** and **15**, respectively, with C(5) as the spiro atom. The reaction with the unsymmetrically substituted 1,3-thiazole-5(4*H*)-thione **14d** occurs with high stereoselectivity from the less hindered side. The addition of the unsymmetrical azomethine ylide **1c** (R = Me) with **14** proceeds less selectively, yielding two regioisomeric cycloadducts **16** and **17**. In the case of **16**, in which the methyl group is close to the spiro-center, the stereoisomer with the methyl group *anti* to the disubstituted C(5) of the dihydro-1,3-thiazole ring is formed exclusively. On the other hand, the regioisomeric cycloadduct **17** is obtained as a mixture of diastereoisomers.

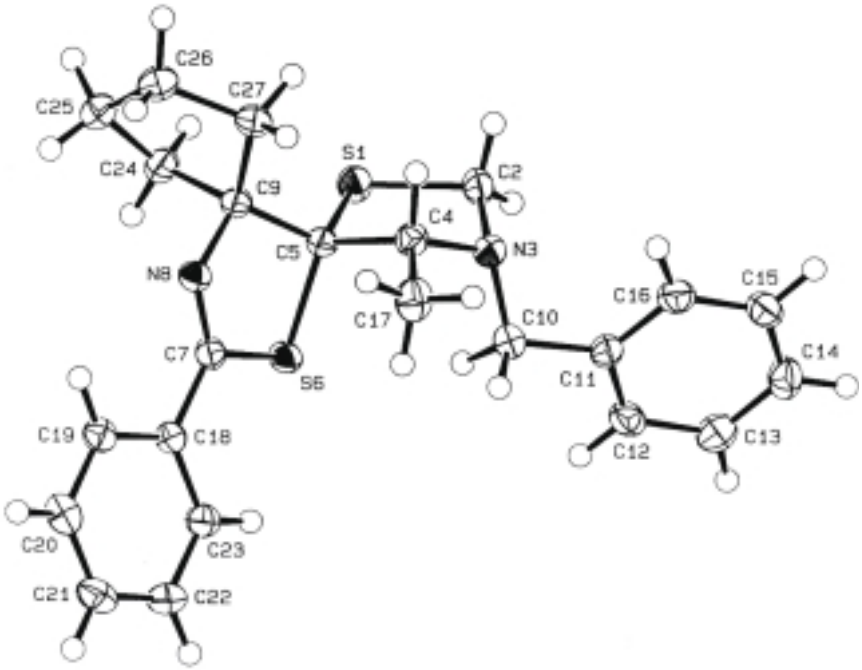


Figure 3. ORTEP plot [34] of the molecular structure of **16b** (arbitrary numbering of atoms; 50% probability ellipsoids).

The described reactions fit well into the series of our recently published results concerning the synthesis of 1,3-thiazolidine derivatives by [2+3]-cycloadditions of azomethine ylides and C=S compounds. The substitution pattern in the product can be varied broadly by using different precursors of the azomethine ylide. Whereas the thermal ring opening of aziridines (see Scheme 1) is well suited for the generation of C- and N-substituted azomethine ylides and, therefore, N-substituted 1,3-thiazolidines and 1,3-thiazolidine carboxylates [25–29], the prototropic 1,2-H shift in imines of α-aminoesters and the formation of metallo-azomethine ylides by treatment with LiBr and DBU, respectively, allow the synthesis of N-unsubstituted 1,3-thiazolidine-5-carboxylates [30]. Furthermore, N-unsubstituted azomethine ylides without electron-withdrawing groups, leading to N-unsubstituted 1,3-thiazolidines, are conveniently generated from *N*-arylidene[(trimethylsilyl)methyl]amines *via* N-silylation/C-desilylation by treatment with a mixture of trimethylsilyl triflate and CsF [31,32]. The fluoride-catalyzed elimination of the Me_3Si and MeO group from **5a**, accelerated by sonification with ultrasound, now makes it possible to prepare 3-benzyl-1,3-thiazolidines without substituents at C(2) and C(4).

EXPERIMENTAL

General. See ref. [27,30]. M.p.'s were determined on a Mettler-FP-5 apparatus and are not corrected. Unless otherwise stated, IR spectra were recorded with a Perkin-Elmer FT-IR-1600 spectrophotometer (in KBr or as film), and NMR-spectra were recorded in $CDCl_3$ on a Bruker-AC-300 (^1H, 300 MHz) or a Bruker-ARX-300 (^{13}C, 75.6 MHz) instrument. CI-MS (with NH_3) were recorded with a

Finnigan-Mat-90- or Finnigan-SSQ-700 spectrometer. Sonification with ultrasound was carried out using an Ultraschall-Busterhorn of the company Branson-Sonifier.

Starting materials. The thiocarbonyl compounds were prepared according to known procedures: Adamantanethione (**10**) [38], 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**12**), and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**13**) by thionation of adamantanone and 2,2,4,4-tetramethylcyclobutane-1,3-dione, respectively, with P_4S_{10} in pyridine [39], and 9*H*-xanthene-9-thione (**11**) by thionation of the corresponding ketone with Lawesson reagent [40]. 4,4-Dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**14a**), 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione (**14b**), and 2-benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**14c**) were prepared according to [41–43]. The synthesis of the enantiomerically pure (*R*)-**14d** has been published recently [31]. *N*-Benzyl-*N*-methoxymethyl-*N*-[1-(trimethylsilyl)alkyl]amines (**5a**,**b**) were prepared from *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine and *N*-benzyl-*N*-[1-(trimethylsilyl)ethyl]amine, respectively, and formaldehyde, according to ref. [44].

Reactions of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (5a) with thioketones. *General procedure.* LiF (30 mg, 1.15 mmol) was added to a solution of the respective thioketone (0.5 mmol) and **5a** (237 mg; 1 mmol) in MeCN (10 ml). The flask was closed and the mixture was sonificated with ultrasound until no thioketone could be detected by TLC. After cooling to rt, the mixture was filtered through Celite and washed with MeCN. Then, the solvent was evaporated and the residue was separated by column chromatography (SiO_2, hexane/AcOEt 20:1).

3′-Benzylspiro[adamantane-2,5′-(1,3-thiazolidine)] (**9a**). From 91 mg (0.51 mmol) of adamantanethione (**10**): 111 mg (74%); colorless crystals. M.p. 53–54°C. IR (KBr): 2967*m*, 2912*s*, 2856*s*, 1599*m*, 1493*m*, 1451*s*, 1365*m*, 1352*m*, 1337*m*, 1305*m*, 1250*s*, 1225*s*, 1123*m*, 1100*m*, 1083*s*, 1064*m*, 1044*s*, 1026*m*, 1001*m*, 987*m*, 946*s*, 903*m*, 875*m*, 865*m*, 838*m*, 800*m*, 736*s*, 722*s*, 696*s*. ^{1}H-NMR: 7.34–7.19 (*m*, 5 arom. H); 3.83 (*s*, $H_2C(2')$); 3.76 (*s*, $PhCH_2$); 2.94 (*s*, $H_2C(4')$); 2.09–1.70 (*m*, 14 H). ^{13}C-NMR: 138.9 (*s*, 1 arom. C); 128.8, 128.3, 127.1 (3*d*, 5 arom. CH); 68.0 (*s*, C(2)); 65.9, 58.9, 58.1 (3*t*, C(2′), $PhCH_2$, C(4′)); 39.8 (*d*, 2 CH); 38.1, 36.9, 35.4 (3*t*, 5 CH_2); 27.0, 26.5 (2*d*, 2 CH). CI-MS: 302 (5), 301 (19), 300 (100, $[M+1]^+$), 266 (10). Suitable crystals for the crystal-structure determination were obtained from i-PrOH/CH_2Cl_2.

3-Benzylspiro[(1,3-thiazolidine)-5,9′-xanthene] (**9b**). From 105 mg (0.5 mmol) of 9H-xanthene-9-thione (**11**): 148 mg (86%); yellow oil. IR (film): 2924m, 2853m, 1657s, 1607s, 1480s, 1459s, 1345s, 1332s, 1239m, 1215m, 1146s, 1100m, 1031m, 933m, 882m, 670m. ^{1}H-NMR: 8.08 (dd, J = 7.9, 1.7, 2 arom. H); 7.28–7.07 (m, 9 arom. H); 6.98 (dd, J = 8.1, 1.4, 2 arom. H); 4.16 (s, $H_2C(2)$); 3.73 (s, $PhCH_2$); 3.13 (s, $H_2C(4)$). ^{13}C-NMR: 150.2, 137.9 (2s, 3 arom. C); 130.0, 128.5, 127.4, 123.1, 116.0 (5d, 13 arom. CH); 126.4 (s, 2 arom. C); 75.4 (t, C(2)); 59.8, 58.4 (2t, $PhCH_2$, C(4)); 57.9 (s, C(5)). CI-MS: 348 (7), 347 (24), 346 (100, $[M+1]^+$), 328 (10), 198 (15), 197 (54), 153 (5).

7-Benzyl-1,1,3,3-tetramethyl-5-thia-7-azaspiro[3.4]octan-2-one (**9c**). From 78 mg (0.50 mmol) of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**12**): 110 mg (76%); colorless oil. The crude material was purified by prep. TLC (hexane/AcOEt 25:1). IR (Film): 2968s, 2928s, 2868s, 2803s, 1776s, 1676s, 1495m, 1454s, 1380m, 1365m, 1316m, 1267s, 1206m, 1172m, 1114s, 1074m, 1028s, 976m, 939m, 911m, 863m, 737s, 700s. ^{1}H-NMR: 7.33-7.26 (m, 5 arom. H); 3.78 (s, $H_2C(6)$); 3.66 (s, $PhCH_2$); 3.06 (s, $H_2C(8)$); 1.30, 1.17 (2s, 2 Me). ^{13}C-NMR: 221.5 (s, C=O); 138.1 (s, 1 arom. C); 128.6, 128.3, 127.4 (3d, 5 arom. CH); 65.6 (s, C(4)); 62.8 (s, C(1), C(3)); 61.5, 58.8, 57.7 (3t, C(6), $PhCH_2$, C(8)); 24.4, 20.1 (2q, 4 Me). CI-MS: 292 (5), 291 (18), 290 (100, $[M+1]^+$).

7-Benzyl-1,1,3,3-tetramethyl-5-thia-7-azaspiro[3.4]octane-2-thione (**9d**). From 87 mg (0.50 mmol) of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**13**): 98 mg (65%); orange oil. In addition, 23 mg (11%) of **9e** were isolated as a minor product. Data of **9d**: IR (film): 2968s, 2926s, 2862s, 2805s, 1656s, 1604m, 1586m, 1495s, 1465s, 1453s, 1375s, 1349s, 1302s, 1245s, 1207s, 1144s, 1114s, 1074s, 1052s, 1027s, 1001m, 957m, 924m, 877m, 860m, 834m, 742s, 699s. ^{1}H-NMR: 7.24–7.13 (m, 5 arom. H); 3.67 (s, $H_2C(6)$); 3.57 (s, $PhCH_2$); 2.98 (s, $H_2C(8)$); 1.27 (s, 2 Me); 1.11 (s, 2 Me). ^{13}C-NMR: 284.3 (s, C=S); 138.2 (s, 1 arom. C); 128.7, 128.4, 127.4 (3d, 5 arom. CH); 69.6 (s, C(4)); 66.0 (s, C(1), C(3)); 62.1, 58.9, 57.8 (3t, C(6), $PhCH_2$, C(8)); 28.8, 23.9 (2q, 4 Me). CI-MS: 308 (11), 307 (19), 306 (100, $[M+1]^+$), 290 (13).

3,10-Dibenzyl-6,6,12,12-tetramethyl-1,8-dithia-3,10-diazadispiro[4.1.4.1]dodecane (**9e**). The reaction of 173 mg (1 mmol) of dithione **13** with 950 mg (4 mmol) of **5a** yielded 293 mg (67%) **9e** as a brownish oil. IR (film): 2966*s*, 1667*s*, 1454*s*, 1251*s*, 1077*s*, 1028*s*, 971*m*, 856*m*, 743*s*, 700*s*. ^{1}H-NMR: 7.37–7.25 (*m*, 10 arom. H); 3.70 (*s*, $H_2C(2)$, $H_2C(9)$); 3.65 (*s*, 2 $PhCH_2$); 2.99 (*s*, $H_2C(4)$, $H_2C(11)$); 1.23

(*s*, 4 Me). ^{13}C-NMR: 137.5 (*s*, 2 arom. C); 128.8, 128.3, 127.4 (3*d*, 10 arom. CH); 69.6 (*s*, C(5), C(7)); 61.4, 58.9, 57.1 (3*t*, 6 CH_2); 47.9 (*s*, C(6), C(12)); 25.4 (*q*, 4 Me). CI-MS: 440 (10), 439 (38, $[M+1]^+$), 391 (8), 347 (9), 324 (11), 323 (21), 322 (100), 307 (8), 306 (54), 276 (6), 233 (6), 220 (8).

Reactions of 5a with 1,3-thiazole-5(4*H*)-thiones. The reactions were carried out according to the *General procedure* described in the previous section.

8-Benzyl-4,4-dimethyl-2-phenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene (**15a**). From 111 mg (0.50 mmol) of 4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-thion (**14a**): 145 mg (82%); colorless crystals. M.p. 60–61°C. IR (KBr): 2982*s*, 2962*s*, 2923*s*, 2843*s*, 1676*m*, 1594*s*, 1574*s*, 1495*s*, 1447*s*, 1379*m*, 1328*m*, 1314*m*, 1306*s*, 1246*s*, 1204*s*, 1171*s*, 1123*m*, 1075*m*, 1064*s*, 1019*s*, 993*s*, 950*s*, 923*s*, 909*s*, 863*m*, 828*s*, 766*s*, 740*s*, 702*s*, 690*s*, 672*s*. ^{1}H-NMR: 8.23 (*d*, *J* = 6.1, 2 arom. H); 7.85–7.65 (*m*, 8 arom. H); 4.53, 4.43 (*AB*, *J* = 8.6, $H_2C(7)$); 4.28, 4.19 (*AB*, *J* = 13.2, $PhCH_2$); 3.91, 3.62 (*AB*, *J* = 12.3, $H_2C(9)$); 2.08, 1.79 (2*s*, 2 Me). ^{13}C-NMR: 165.6 (*s*, C=N); 138.6, 133.5 (2*s*, 2 arom. C); 131.1, 128.8, 128.5, 128.4, 128.0, 127.5 (6*d*, 10 arom. CH); 87.1 (*s*, C(5)); 81.2 (*s*, C(4)); 66.4 (*t*, C(7)); 61.3 (*t*, $PhCH_2$); 57.9 (*t*, C(9)); 25.0, 22.3 (2*q*, 2 Me). CI-MS: 357 (11), 356 (24), 355 (100, $[M+1]^+$), 241 (7), 240 (41), 208 (10).

3-Benzyl-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.3.4]tridec-11-ene (**15b**). From 126 mg (0.51 mmol) of 2-phenyl-3-thia-1-azaspiro[4.4]non-2-ene (**14b**): 160 mg (84%); colorless crystals. M.p. 103–104°C. IR (KBr): 2955*s*, 2838*s*, 1726*m*, 1668*s*, 1591*s*, 1487*s*, 1446*s*, 1360*s*, 1319*s*, 1245*s*, 1176*m*, 1127*s*, 1076*m*, 1025*m*, 1006*s*, 978*m*, 963*m*, 944*s*, 925*s*, 825*s*, 747*s*, 770*s*, 692*s*, 669*m*. ^{1}H-NMR: 7.81 (*d*, *J* = 6.4, 2 arom. H); 7.46–7.25 (*m*, 8 arom. H); 4.17, 4.10 (*AB*, *J* = 8.8, $H_2C(2)$); 3.93, 3.84 (*AB*, *J* = 13.2, $PhCH_2$); 3.57, 2.27 (*AB*, *J* = 12.4, $H_2C(4)$); 2.26–2.17 (*m*, 1 H); 2.08–1.87 (*m*, 4 H); 1.83–1.75 (*m*, 3 H). ^{13}C-NMR: 165.1 (*s*, C=N); 138.1, 133.7 (2*s*, 2 arom. C); 131.1, 128.6, 128.4, 128.3, 128.1, 127.5 (6*d*, 10 arom. CH); 92.3 (*s*, C(5)); 85.5 (*s*, C(6)); 67.2 (*t*, C(2)); 61.5 (*t*, $PhCH_2$); 58.1 (*t*, C(4)); 37.7, 34.3, 25.4, 24.5 (4*t*, 4 CH_2). CI-MS: 383 (11), 382 (24), 381 (100, $[M+1]^+$), 133 (15).

2,8-Dibenzyl-4,4-dimethyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene (**15c**). From 115 mg (0.49 mmol) of 2-benzyl-4,4-dimethyl-1,3-thiazol-5(4*H*)-thion (**14c**): 146 mg (79%); colorless oil. IR (film): 2974*s*, 1667*s*, 1534*s*, 1494*s*, 1453*s*, 1383*m*, 1361*m*, 1119*m*, 1029*m*, 846*m*, 740*m*, 699*s*. ^{1}H-NMR: 7.41–7.23 (*m*, 10 arom. H); 4.09, 4.00 (*AB*, *J* = 8.7, $H_2C(7)$); 3.83, 3.77 (*AB*, *J* = 14.8, $PhCH_2$); 3.75, 3.66 (*AB*, *J* = 13.2, $PhCH_2$); 3.39, 3.14 (*AB*, *J* = 12.4, $H_2C(9)$); 1.57, 1.29 (2*s*, 2 Me). ^{13}C-NMR: 168.2 (*s*, C=N); 138.1, 135.7 (2*s*, 2 arom. C); 128.9, 128.8, 128.7, 128.5, 127.4, 127.1 (6*d*, 10 arom. CH); 87.8 (*s*, C(5)); 80.5 (*s*, C(4)); 66.3 (*t*, C(7)); 61.3, 57.8 8 (2*t*, 2 $PhCH_2$); 41.5 (*t*, C(9)); 24.9, 22.2 (2*q*, 2 Me). CI-MS: 371 (8), 370 (17), 369 (100, $[M+1]^+$).

*(4*R*,5*R*)-4,8-Dibenzyl-4-methyl-2-phenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**15d**). From 149 mg (0.50 mmol) of (*R*)-4-benzyl-4-methyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**14d**): 163 mg (76%); colorless oil. IR (film): 2931*s*, 1708*s*, 1592*s*, 1493*s*, 1446*s*, 1365*m*, 1309*m*, 1242*m*, 1173*m*, 1121*m*, 1076*m*, 1027*m*, 1015*m*, 1000*s*, 953*s*, 847*m*, 765*m*, 735*m*, 691*m*, 672*m*. ^{1}H-NMR: 7.83–7.81 (*m*, 2 arom. H); 7.48–7.20 (*m*, 13 arom. H); 4.21, 4.11 (*AB*, *J* = 8.7, $H_2C(7)$); 3.91, 3.83 (*AB*, *J* = 13.1, $PhCH_2$); 3.75, 2.86 (*AB*, *J* = 13.4, $PhCH_2$); 3.53, 3.26 (*AB*, *J* = 12.3, $H_2C(9)$); 1.22 (*s*, Me). ^{13}C-NMR: 165.9 (*s*, C=N); 138.2, 137.9, 133.4 (3*s*, 3 arom. C); 131.1, 128.8, 128.4, 128.3, 128.2, 127.6, 127.5, 126.2 (8*d*, 15 arom. CH); 87.8 (*s*, C(5)); 83.2 (*s*, C(4)); 66.6 (*t*, C(7)); 61.4, 58.0 (2*t*, 2 $PhCH_2$); 43.6 (*t*, C(9)); 25.2 (*q*, Me). CI-MS: 432 (23), 431 (100, $[M+1]^+$). Suitable crystals for the crystal-structure determination were grown from i-PrOH/MeOH. $[\alpha]_D$ = +40.7 (c = 1.6, $CHCl_3$).

Reactions of *N*-benzyl-*N*-(methoxymethyl)-*N*-[1-(trimethylsilyl)ethyl]amin (5b) with 1,3-thiazole-5(4*H*)-thiones. The reactions were carried out according to the *General procedure* described above. Chromatography (SiO_2, hexane/AcOEt) gave a pure adduct **16** (more polar fraction) and a mixture of diastereoisomers **17** (less polar fraction).

*(5*RS*,9*RS*)-8-Benzyl-4,4,9-trimethyl-2-phenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**16a**). From 111 mg (0.50 mmol) of **14a**; more polar fraction: 37 mg (20%); yellowish oil. IR (film): 2963*m*, 2871*s*, 1708*s*, 1589*s*, 1572*m*, 1491*m*, 1439*m*, 1376*m*, 1320*m*, 1257*m*, 1141*s*, 1079*m*, 1025*m*, 990*s*, 931*m*, 849*m*. ^{1}H-NMR: 7.84–7.81 (*m*, 2 arom. H); 7.47–7.26 (*m*, 8 arom. H); 3.95, 3.78 (*AB*, *J* = 8.2, $H_2C(7)$); 3.92, 3.70 (*AB*, *J* = 13.4, $PhCH_2$); 3.33 (*q*, *J* = 6.4, HC(9)); 1.59 (*s*, Me_2C); 1.44 (*d*, *J* = 6.4, MeC(9)). ^{13}C-NMR: 163.9 (*s*, C=N); 138.6, 133.1 (2*s*, 2 arom. C); 130.4, 127.7, 127.5, 127.4, 126.9, 126.3 (6*d*, 10 arom. CH); 88.8, 79.6 (2*s*, C(4), C(5)); 67.0 (*d*, C(9)); 55.9, 52.3 (2*t*, C(7), $PhCH_2$); 26.2, 20.9, 12.3 (3*q*, 3 Me). CI-MS: 371 (12), 370 (24), 369 (100, $[M+1]^+$).

*(5*RS*,7*RS*)-* and *(5*RS*,7*SR*)-8-Benzyl-4,4,7-trimethyl-2-phenyl-1,6-dithia-3,8-diazaspiro-[4.4]non-2-ene* (**17a**). From 111 mg (0.50 mmol) of **14a**; less polar fraction; 1:2-mixture of diastereoisomers: 72 mg (39%); yellowish oil. IR (film): 2965*m*, 2870*s*, 1703*m*, 1591*s*, 1570*m*, 1490*s*, 1441*s*, 1376*m*, 1324*s*, 1312*m*, 1256*s*, 1141*s*, 1075*m*, 1027*s*, 997*m*, 930*m*, 694*m*. ^{1}H-NMR (2 diastereoisomers): 7.81–7.75 (*m*, 2 arom. H); 7.74–7.22 (*m*, 8 arom. H); 4.50 (*q*, *J* = 6.4, HC(7)); 4.27 (*q*, *J* = 6.0, HC(7)); 3.98, 3.60 (*AB*, *J* = 13.7, $PhCH_2$); 3.97, 3.69 (*AB*, *J* = 13.4, $PhCH_2$); 3.66, 3.38 (*AB*, *J* = 12.8, $H_2C(9)$); 3.40, 3.00 (*AB*, *J* = 11.0, $H_2C(9)$); 1.62, 1.57 (2*s*, Me_2C); 1.53 (*d*, *J* = 6.0, MeC(7)); 1.42 (*d*, *J* = 6.4, MeC(7)); 1.35 (*s*, Me_2C). ^{13}C-NMR (2 diastereoisomers): 165.6, 164.9 (2*s*, C=N); 138.9, 137.5, 132.4, 132.3 (4*s*, 2 arom. C); 130.3, 130.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.3, 126.8 (12*d*, 10 arom. CH); 86.1, 83.9 (2*s*, C(4)); 80.0, 78.6 (2*s*, C(5)); 71.4, 68.0 (2*d*, C(7)); 65.1, 63.6 (2*t*, $PhCH_2$); 58.4, 54.3 (2*t*, C(9)); 25.6, 25.1, 23.3, 22.6, 22.4, 19.9 (6*q*, 6 Me). CI-MS: 383 (11), 371 (11), 370 (26), 369 (100, $[M+1]^+$).

*(4*RS*,5*RS*)-3-Benzyl-4-methyl-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]non-11-ene* (**16b**). From 124 mg (0.50 mmol) of **15b**; more polar fraction: 37 mg (19%); yellow oil. IR (film): 2965*s*, 2872*s*, 1666*m*, 1593*s*, 1574*s*, 1494*s*, 1447*s*, 1377*m*, 1312*s*, 1255*s*, 1116*s*, 1075*m*, 1027*s*, 1001*s*, 950*s*, 909*s*, 830*m*, 613*m*. ^{1}H-NMR: 7.73 (*d*, *J* = 6.3, 2 arom. H); 7.37–7.13 (*m*, 8 arom. H); 3.86, 3.73 (*AB*, *J* = 8.4, $H_2C(2)$); 3.79, 3.64 (*AB*, *J* = 13.4, $PhCH_2$); 3.17 (*q*, *J* = 6.4, HC(4)); 2.05–1.62 (*m*, 4 CH_2); 1.34 (*d*, *J* = 6.4, Me). ^{13}C-NMR: 164.7 (*s*, C=N); 138.0, 132.7 (2*s*, 2 arom. C); 131.0, 128.6, 128.4, 128.3, 127.8, 127.1 (6*d*, 10 arom. CH); 89.7, 86.7 (2*s*, C(5), C(6)); 68.0 (*d*, C(4)); 56.7, 51.9 (2*t*, C(2), $PhCH_2$); 40.3, 31.2, 23.8, 22.5 (4*t*, 4 CH_2); 12.5 (*q*, Me). CI-MS: 397 (10), 396 (25), 395 (100, $[M+1]^+$), 242 (5), 184 (26). Suitable crystals for the crystal-structure determination were grown from i-PrOH/$CHCl_3$.

*(2*RS*,5*RS*)-* and *(2*RS*,5*SR*)-3-Benzyl-2-methyl-12-phenyl-1,13-dithia-3,11-diazadispiro-[4.0.4.3]non-11-ene* (**17b**). From 124 mg (0.50 mmol) of **14b**; less polar fraction; 1:2-mixture of diastereoisomers: 84 mg (43%); yellow oil. IR (film): 2967*s*, 2871*s*, 1701*m*, 1591*s*, 1573*s*, 1493*s*, 1441*s*, 1376*s*, 1325*s*, 1312*m*, 1255*s*, 1175*m*, 1140*s*, 1075*m*, 1027*s*, 1000*s*, 952*s*, 908*s*, 828*m*, 693*s*. ^{1}H-NMR (2 diastereoisomers): 7.71–7.66 (*m*, 2 arom. H); 7.34–7.11 (*m*, 8 arom. H); 4.39 (*q*, *J* = 6.4, HC(2)); 4.22 (*q*, *J* = 6.0, HC(2)); 3.92, 3.65 (*AB*, *J* = 13.4, $PhCH_2$); 3.89, 3.50 (*AB*, *J* = 13.7, $PhCH_2$); 3.55, 3.30 (*AB*, *J* = 12.8, $H_2C(4)$); 3.36, 2.89 (*AB*, *J* = 11.2, $H_2C(4)$); 2.03–1.62 (*m*, 8 H); 1.44 (d, *J* = 6.0, Me); 1.33 (d, *J* = 6.4, Me). ^{13}C-NMR (2 diastereoisomers): 164.5, 164.1 (2*s*, C=N); 137.8, 137.3, 132.9, 132.8 (4*s*, 2 arom. C); 131.0, 130.2, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.3, 127.2, 126.9 (12*d*, 10 arom. CH); 91.0, 89.7, 88.2, 84.7 (4*s*, C(5), C(6)); 70.3, 67.4 (2*d*, C(2)); 66.9, 65.8 (2*t*, $PhCH_2$); 63.9, 57.8 (2*t*, C(4)); 33.1, 32.6, 24.2, 24.1, 23.4, 23.3, 22.9, 18.8 (8*t*, 4 CH_2). CI-MS: 397 (11), 396 (26), 395 (100, $[M+1]^+$), 323 (10), 208 (5).

Crystal structure determination of 9a, 15d, and 16b[*]. All measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Data collection and refinement parameters are given in the Table, views of the molecules are shown in Figures 1–3. The structures were solved by direct methods using SHELXS86 [45] in the case of **9a** and **16b** and SIR92 [46] in the case of **15d**, which, in each case, revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. In the case of **9a** and **16b**, all of the H-atoms were located in a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. In the case of **15d**, all of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å) and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimised the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$. A correction for secondary extinction was applied in the case of **15d**. For **15d**, refinement of the absolute structure parameter [47] yielded a value of 0.03(6), which confirms that the refined coordinates represent the true enantiomorph. This is in accordance with the expected (*R*)-configuration at C(9). Neutral atom scattering factors for the non-hydrogen atoms were taken from

[*]CCDC-198100–198102 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk).

[48a], and the scattering factors for H-atoms were taken from [49]. Anomalous dispersion effects were included in F_{calc} [50]; the values for f' and f'' were those of [48b]. The values of the mass attenuation coefficients are those of [48c]. All calculations were performed using the TEXSAN [51] (for **9a** and **16b**) or teXsan [52] (for **15d**) crystallographic software package.

Table. Crystallographic data for compounds **9a**, **15d**, and **16b**.

	9a	**15d**	**16b**
Crystallized from	*i*-PrOH/CH_2Cl_2	*i*-PrOH/MeOH	*i*-PrOH/$CHCl_3$
Empirical formula	$C_{19}H_{25}NS$	$C_{26}H_{26}N_2S_2$	$C_{23}H_{26}N_2S_2$
Formula weight [g/mol]	299.47	430.62	394.59
Crystal color, habit	colorless, prism	colorless, needle	colorless, prism
Crystal dimensions [mm]	0.18×0.33×0.40	0.18×0.25×0.43	0.28×0.40×0.45
Temperature [K]	173(1)	173(1)	173(1)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12$	$P2_1/c$
Z	4	4	4
Reflections for cell determination	25	24	25
2θ range for cell determination [°]	37–40	33–40	38–40
Unit cell parameters a [Å]	11.966(3)	15.127(4)	8.100(2)
b [Å]	7.183(2)	21.617(3)	14.083(2)
c [Å]	18.479(2)	6.930(2)	17.964(2)
β [°]	93.79(1)	90	98.14(1)
V [Å^3]	1584.7(5)	2266.1(9)	2028.5(6)
D_x [g cm^{-3}]	1.255	1.262	1.292
μ(MoK_α) [mm^{-1}]	0.198	0.250	0.273
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	55	60
Total reflections measured	4123	5707	6528
Symmetry independent reflections	3645	4980	5908
Reflections used [$I > 2\sigma(I)$]	2892	4266	4078
Parameters refined	290	273	348
Final R	0.0393	0.0381	0.0451
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0379	0.0352	0.0376
Goodness of fit	1.823	1.465	1.761
Secondary extinction coefficient	–	$3.9(3)\times10^{-7}$	–
Final Δ_{max}/σ	0.0006	0.0005	0.0006
$\Delta\rho$ (max; min) [e/Å^3]	0.27; –0.24	0.21; –0.17	0.37; –0.29

Acknowledgments

We thank the analytical units of our Institute for the spectra, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

REFERENCES

1. Grigg R. and Sridharan V., in "Advances in Cycloaddition", ed. Curran D.P., JAI Press, Greenwich, 1993, Vol. 3, p. 161.
2. Harwood L.M. and Vickers R.J., in "Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products", eds. Padwa A. and Pearson W.H., J. Wiley & Sons, NY, 2002, p. 169.
3. Clark J.S., in "Nitrogen, Oxygen and Sulfur Ylide Chemistry, A Practical Approach", ed. Clark J.S., Oxford University Press, 2002, p. 57.
4. Cooper D.M., Grigg R., Hargreaves S., Kennewell P. and Redpath J., *Tetrahedron*, **51**, 7791 (1995).
5. Alcaide B., Almendros P., Alonso J.M. and Aly M.F., *Chem. Commun.*, 485 (2000).
6. Merino I., Santosh Laxmi Y.R., Florez J., Barluenga J., Ezquerra J. and Pedregal C., *J. Org. Chem.*, **67**, 648 (2002); Garcia Ruano J.L., Tito A. and Peromingo M.T., *J. Org. Chem.*, **67**, 981 (2002).
7. Stuhlmann F. and Kaufmann D.E., *J. Prakt. Chem.*, **341**, 455 (1999).
8. Pandey G., Sahoo A.K., Gadre S.R., Bagul T.D. and Phalgune U.D., *J. Org. Chem.*, **64**, 4990 (1999).
9. Martel S.R., Wisedale R., Gallagher T., Hall L.D., Mahon M.F., Bradbury R.H. and Hales N.J., *J. Am. Chem. Soc.*, **119**, 2309 (1997).
10. Obst U., Betschmann P., Lerner C., Seiler P., Diederich F., Gramlich V., Weber L., Banner D.W. and Schönholzer P., *Helv. Chim. Acta*, **83**, 855 (2000).
11. Planchenault D., Wisedale R., Gallagher T. and Hales N.J.,*J. Org. Chem.*, **62**, 3438 (1997); Gallagher T., *J. Heterocycl. Chem.*, **36**, 1365 (1999).
12. La Porta P., Capuzzi L. and Bettarini F., *Synthesis*, 287 (1994).
13. Coldham I., Collis A.J., Mould R.J. and Robinson D.E., *Synthesis*, 1147 (1995).
14. Matsumoto K., Ohta R., Uchida T., Nishioka H., Yoshida M. and Kakehi A., *J. Heterocycl. Chem.*, **32**, 367 (1995).
15. Gonzales G., Martin M.V. and Paredes M.C., *Heterocycles*, **52**, 237 (2000).
16. Barr D.A., Dorrity M.J., Grigg R., Hargreaves S., Malone J.F., Montgomery J., Redpath J., Stevenson P. and Thornton-Pett M., *Tetrahedron*, **51**, 273 (1995).
17. Terao Y., Aono M. and Achiwa K., *Heterocycles*, **27**, 981 (1988).
18. Padwa A. and Dent W., *J. Org. Chem.*, **52**, 235 (1987); Padwa A., Eisenbarth P., Venkatramanan M.K. and Wong G.S.K., *J. Org. Chem.*, **52**, 2427 (1987).
19. Imai N., Terao Y., Achiwa K. and Sekiya M., *Tetrahedron Lett.*, **25**, 1579 (1984).
20. Confalone P.N. and Huie E.M., *J. Am. Chem. Soc.*, **106**, 7175 (1984).
21. Tsuge O., Kanemasa S., Ohe M. and Takenaka S., *Bull. Chem. Soc. Jpn.*, **60**, 4079 (1987).
22. Beugelmans R., Chastanet J. and Roussi G., *Heterocycles*, **26**, 3197 (1987).
23. Padwa A. and Hornbuckle S.F., *Chem. Rev.*, **91**, 263 (1991); Padwa A. and Weingarten M.D., *Chem. Rev.*, **96**, 223 (1996).
24. Rasmussen K.G. and Jorgensen K.A., *J. Chem. Soc., Perkin Trans. 1*, 1287 (1997).
25. Mlostoń G. and Skrzypek Z., *Bull. Soc. Chim. Belg.*, **99**, 167 (1990).
26. Mlostoń G., Linden A. and Heimgartner H., *Polish J. Chem.*, **71**, 32 (1997); *Helv. Chim. Acta*, **81**, 558 (1998).
27. Gebert A., Linden A., Mlostoń G. and Heimgartner H., *Heterocycles*, **56**, 393 (2002).
28. Mlostoń G., Urbaniak K. and Heimgartner H., *Helv. Chim. Acta*, **85**, 2056 (2002).
29. Mlostoń G., Urbaniak K., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **85**, 2644 (2002).
30. Gebert A., Linden A. and Heimgartner H., *Heterocycles*, **54**, 691 (2001).
31. Gebert A. and Heimgartner H., *Helv. Chim. Acta*, **85**, 2073 (2002).
32. Gebert A., Linden A., Mlostoń G. and Heimgartner H., *Polish J. Chem.*, **77**, 157 (2003).
33. Suslick K.S., "Ultrasound", VCH Publisher Inc., NY, 1988.

34. Johnson C.K., "ORTEPII", Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
35. Heimgartner H., *Croat. Chem. Acta*, **59**, 237 (1986); Heimgartner H., *Phosphorus, Sulfur, and Silicon*, **58**, 281 (1991).
36. Mlostoń G., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **74**, 1386 (1991).
37. Kägi M., Linden A., Heimgartner H. and Mlostoń G., *Helv. Chim. Acta*, **76**, 1715 (1993); Mlostoń G., Petit M., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **77**, 435 (1994); Kelmendi B., Mlostoń G. and Heimgartner H., *Heterocycles*, **52**, 475 (2000).
38. Greidanus J.W., *Can. J. Chem.*, **48**, 3530 (1970).
39. Mlostoń G., Romański J., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **76**, 2147 (1993).
40. Pedersen B.S., Scheibye S., Nilsson N.H. and Lawesson S.-O., *Bull. Soc. Chim. Belg*., **87**, 223 (1978).
41. Obrecht D., Prewo R., Bieri J.H. and Heimgartner H., *Helv. Chim. Acta*, **65**, 1825 (1982).
42. Jenny C. and Heimgartner H., *Helv. Chim. Acta*, **69**, 374 (1986).
43. Tromm P. and Heimgartner H., *Helv. Chim. Acta*, **71**, 2071 (1988).
44. Padwa A., Chen Y.-Y., Dent W. and Nimmesgern H., *J. Org. Chem*., **50**, 4006 (1985).
45. Sheldrick G.M., "SHELXS86", *Acta Cryst. A* , **46**, 467 (1990).
46. Altomare A., Cascarano G., Giacovazzo C., Guagliardi A., Burla M.C., Polidori G. and Camalli M., "SIR92", *J. Appl. Cryst.*, **27**, 435 (1994).
47. a) Flack H.D. and Bernardinelli G., *Acta Cryst. A*, **55**, 908 (1999); b) Flack H.D. and Bernardinelli G., *J. Appl. Cryst.*, **33**, 1143 (2000).
48. a) Maslen E.N., Fox A.G. and O'Keefe M.A., in "International Tables for Crystallography", ed. Wilson A.J.C., Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477; b) Creagh D.C. and McAuley W.J., in "International Tables for Crystallography", ed. Wilson A.J.C., Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219; c) Creagh D.C. and Hubbell J.H., in "International Tables for Crystallography", ed. Wilson A.J.C., Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, p. 200.
49. Stewart R.F., Davidson E.R. and Simpson W.T., *J. Chem. Phys*., **42**, 3175 (1965).
50. Ibers J.A. and Hamilton W.C., *Acta Cryst.*, **17**, 781 (1964).
51. TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, The Woodlands, Texas, 1989.
52. teXsan: Single Crystal Structure Analysis Software, Version 1.10b, Molecular Structure Corporation, The Woodlands, Texas, 1999.