Pergamon

TETRAHEDRON

Tetrahedron 56 (2000) 6795–6804

Solid-State Photochemistry: Absolute Asymmetric β-Thiolactam Synthesis from Achiral *N*,*N*-Dibenzyl-α,β-unsaturated Thioamides

Masami Sakamoto,[a,*] Masaki Takahashi,[a] Wataru Arai,[a] Takashi Mino,[a] Kentaro Yamaguchi,[b] Shoji Watanabe[a] and Tsutomu Fujita[a]

[a]*Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*
[b]*Chemical Analysis Center, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

Received 25 November 1999; revised 1 February 2000; accepted 8 February 2000

Abstract—Several types of achiral *N*,*N*-dibenzyl-α,β-unsaturated thioamides were subjected to X-ray crystallographic analysis, and it was revealed that methylcrotonthioamide and 1-cyclohexenecarbothioamide provided chiral crystals. The absolute configuration determined by anomalous scattering method corresponded to the cotton effect in the solid-state CD spectra. The solid-state photoreaction gave optically active β-thiolactams. On the other hand, *E*–*Z* isomerization takes place in the photoreaction of a tiglylthioamide derivative. Stereochemical assignment before and after the reaction was rationalized by the hydrogen abstraction by alkenyl carbon followed by cyclization via a zwitterionic intermediate. © 2000 Elsevier Science Ltd. All rights reserved.

The achievement of an asymmetric synthesis starting from an achiral reagent and in the absence of any external chiral agent has long been an intriguing challenge to chemists[1] and is also central to the issue of the origin of optical activity in nature.[2] Stereospecific solid-state chemical reactions of chiral crystals formed by achiral materials are defined as 'absolute' asymmetric synthesis.[3] This situation arises when achiral compounds crystallized by spontaneous resolution undergo reactions in the crystalline lattices generating new stereocenters into the products. Since many solid-state reactions proceed with the least atomic or molecular movement, the X-ray crystallographic approach is very useful to gain insight into the mechanistic features and reactivities. When the molecule in a crystalline lattice can react under topochemical control due to well-defined atomic arrangement, selected and restricted reaction is allowed predominantly and chemoselective or stereoselective reaction is observed in the solid-state reaction.

Since the concept of a topochemically controlled reaction was established by Schmidt,[4] various approaches to asymmetric syntheses using a chiral crystalline environment, especially for intermolecular 2+2 cyclobutane formation have been reported.[5] On the other hand, Scheffer and co-workers described the first example of an intramolecular version of the 'absolute' asymmetric syntheses by means of the photochemical di-π-methane rearrangement and Norrish Type II cyclization.[6] Further investigations concerning intramolecular absolute asymmetric transformations have been reported in the last five years.[7] Considerable efforts have been made in this field; however, variations of the methodology still remain underdeveloped. Recently, we

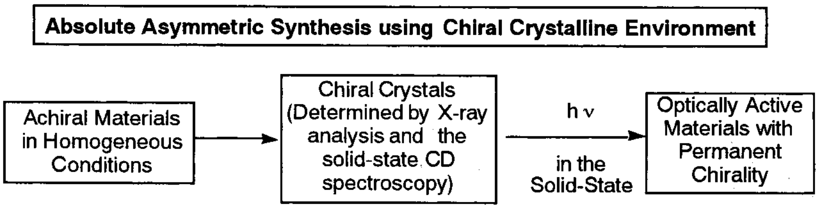

Figure 1.

Keywords: amide; photoreaction; chiral crystal; absolute asymmetric synthesis; solid state.

* Corresponding author. E-mail: saka@galaxy.tc.chiba-u.ac.jp

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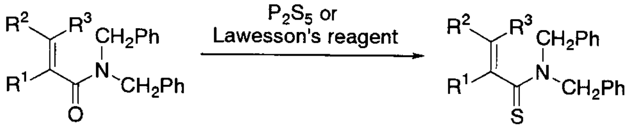
PII: S0040-4020(00)00501-9



	R^1	R^2	R^3
1a	Me	H	Me
1b	H	Me	Me
1c	-$(CH_2)_4$-		H
1d	-$(CH_2)_5$-		H

Scheme 1.

described the solid-state photoreaction of *N*,*N*-dibenzylcyclohexenecarbothioamide, which formed chiral crystals, and led to optically active β-thiolactam with excellent enantioselectivity.[8] The mechanism was explainable in terms of the hydrogen abstraction by an alkenyl double bond from the benzylic position followed by cyclization. To establish the validity and generality of this reaction, we have investigated the solid-state photoreactions of various α,β-unsaturated thioamides (see Fig. 1).

Results and Discussion

The thioamides **1a–1d** were conveniently prepared by thionation of the corresponding *N*,*N*-dibenzyl-α,β-unsaturated amides with Lawesson's reagent or P_2S_5.[9] As for thioamide **1a**, geometric *E*/*Z* isomerization occurs at the C=C double bond during the thionation of (*E*)-*N*,*N*-dibenzyltiglylamides giving *N*,*N*-dibenzyltiglylthioamides **1a** with (*Z*)-configuration, which was unequivocally established by X-ray crystallographic analysis. Recrystallization of each material from the chloroform–hexane solution gave, respectively, colorless or slightly yellowish prismatic crystals (see Scheme 1).

X-Ray crystallographic analysis and the molecular conformation of 1a–1d

All thioamides were subjected to X-ray single crystal analysis. Table 1 summarizes the crystal data. The crystal of **1b**

Table 1. Crystal data for α,β-unsaturated thioamides **1a–1d**

Entry	1a	1b	1c	1d
Formula	$C_{19}H_{21}NS$	$C_{19}H_{21}NS$	$C_{21}H_{23}NS$	$C_{22}H_{25}NS$
Mol. weight	295.44	295.44	321.48	335.51
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_12_12_1$	$P2_1$	$P2_1/n$
Z	4	4	2	4
a (Å)	17.430(4)	13.232(6)	8.760(2)	7.205(10
b (Å)	15.382(4)	17.928(6)	10.262(3)	11.812(2)
c (Å)	6.557(2)	7.125(6)	10.238(3)	22.57(3)
β (°)	99.64(2)	90.00(0)	100.15(2)	92.13(9)
V (Å^3)	1733.1(8)	1690(1)	905.9(4)	1919(4)
ρ_{calc} (g/cm^{-3})	1.13	1.16	1.178	1.161
μ(CuK_α) (cm^{-1})	15.475	16.24	15.55	1.71[a]
F(000)	631	632	344	720
Crystal size (mm)	0.40×0.15×0.15	0.35×0.25×0.10	0.15×0.20×0.32	0.40×0.25×0.18
Used reflections	3177	2200	2367	2489
R	0.043	0.055	0.063	0.097
R_w	0.046	0.062	0.057	0.133

[a] MoK_α was used.

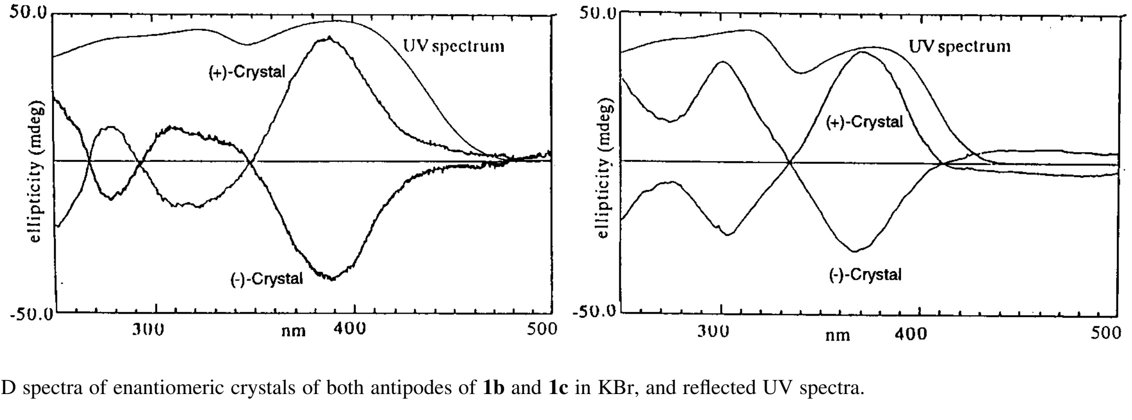


Figure 2. CD spectra of enantiomeric crystals of both antipodes of **1b** and **1c** in KBr, and reflected UV spectra.

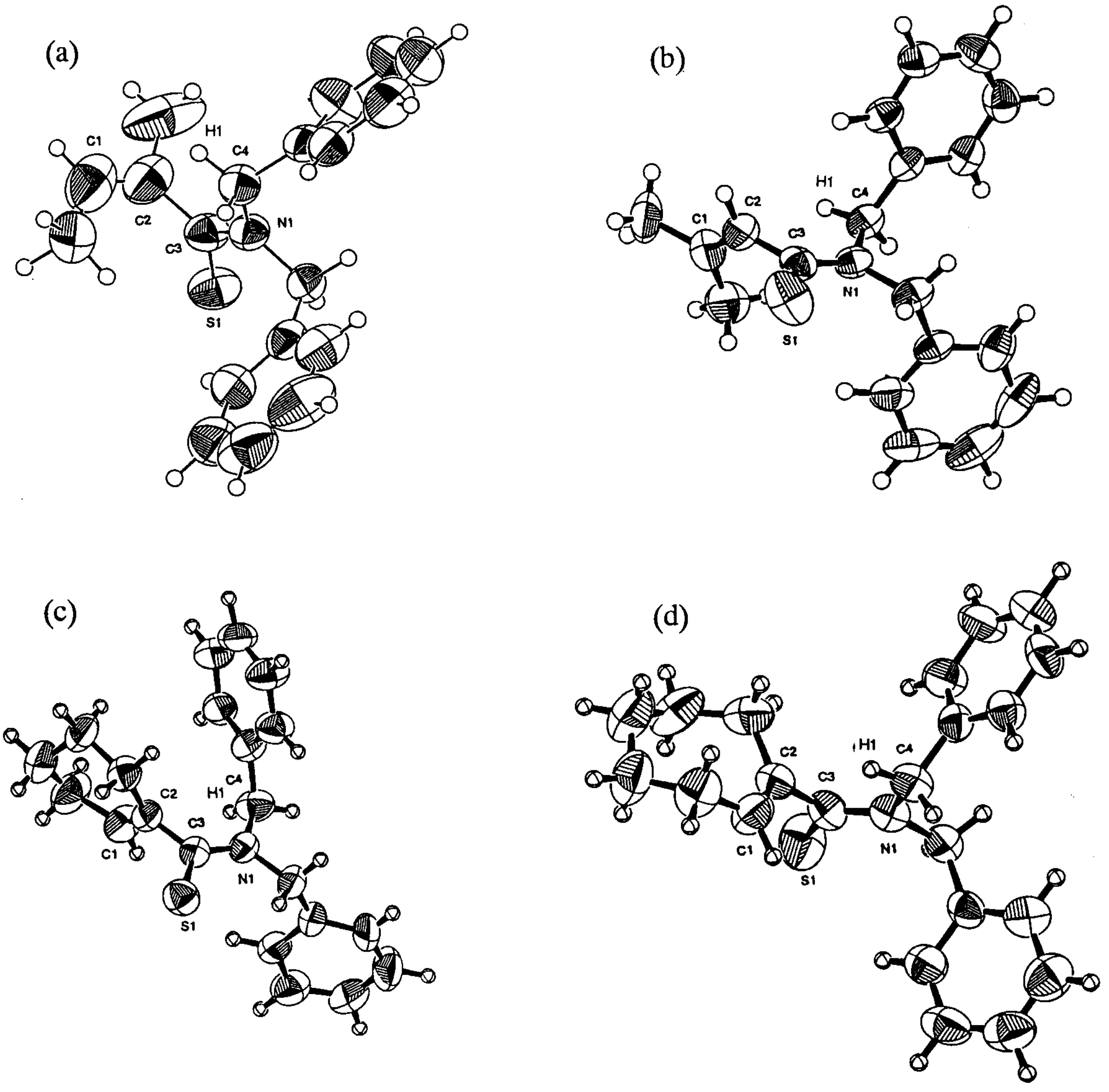
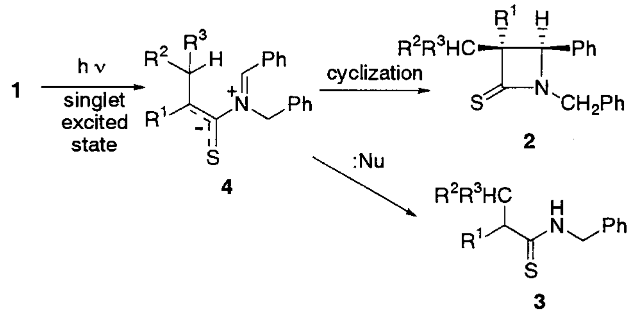


Figure 3. ORTEP drawing of the crystal structure of (a) the racemic crystal of **1a**, (b) the absolute configuration of (+)-**1b**, (c) the absolute configuration of (+)-**1c**, (d) the racemic crystal of **1d**.

showed an orthorhombic crystal system and other crystals (**1a**, **1c**, **1d**) were monoclinic. For the achievement of absolute asymmetric synthesis, achiral materials must crystallize in a chiral space group. Fortunately, 3-methylcrotonoyl and 1-cyclohexene carbonyl derivatives **1b** and **1c** gave a chiral crystal system. Each single crystal is chiral and all molecules in one crystal are optically active, offering the same chiral configuration. Fig. 2 shows the reflected UV and the CD spectra of each of two enantiomorphic crystals of **1b** (Fig. 2b) and **1c** (Fig. 2c) in KBr pellets, which were independently obtained by spontaneous resolution. These crystals gave specific curves in the region between 250 and 450 nm, which were mirror images designated as (+) and (−) at the wavelength of 370 nm. Fig. 3 shows the ORTEP drawing of **1a**–**1d** obtained by X-ray crystallographic analysis. The two ORTEP diagrams of **1b** (Fig. 3b) and **1c** (Fig. 3c) exhibit the absolute structure of the chiral conformation, which was determined by X-ray anomalous scattering method, and corresponded to each (+)-crystal in the solid-state CD spectra (Fig. 2).

When chiral crystals are formed, one question always arises: whether all the crystals in one batch have the same absolute configuration or are a mixture of both enantiomorphic crystals. Except for crystallizations which have been carefully monitored turns out the formation of the former crystals; however, the ratio is not just 50:50, and one enantiomer predominates over the other enantiomorph. On the other hand, slow and careful crystallization resulted in higher probability for the resolution into one enantiomer. In several cases, it is known that the all crystals in one batch show the same chirality.[7] The first generated enantiomorphic crystal works as a seed, and all the crystals in one batch will turn out to have the same absolute configuration. The probability for the rotatory, (+) or (−), should be the same, when the chiral resolution occurs. In the cases of **1b** and **1c**, both optically active chiral crystals were easily obtained by the spontaneous crystallization. Once enantiomorphic crystals are formed, a large amount of the desired chiral crystals can be selectively prepared by seeding the desired crystals through recrystallization (see Table 1).



Scheme 2.

Photochemical reaction of 1a–1d in benzene

Recently, we reported the solution photochemistry for **1a** and **1c**, which gave the corresponding β-thiolactam **2** and debenzylated thioamide **3**.[10] Alkenyl β-carbon can abstract benzylic hydrogen leading to zwitterionic intermediate **4** (Scheme 2). The fact that the zwitterion **4** was the common intermediate for **2** and **3** was confirmed by the reaction, in which irradiation of **1** in the presence of *n*-butylamine as a nucleophile suppressed the amount of **2** and resulted in the increase of the mono-substituted thioamide **3** (Table 2).

Photolysis of other thioamides **1b** and **1d** also gave the corresponding β-thiolactam **2** accompanied with debenzylated *N*-benzylthioamide **3** as shown in Table 2. Two diastereomers were possible for the β-thiolactam **2a** and **2b**; however, only the (*Z*)-isomer was obtained selectively. The stereochemistry was determined on the basis of the chemical shift in the NMR spectra and NOE. Irradiation of the methine singlet (4.60 ppm) at the C-4 position of **2a** exhibited an NOE with 3-methyl singlet, but led to no observable NOE for the 3-ethyl signals as shown in Fig. 4a.

In the stereochemistry of **2b**, an NOE was observed between 3- and 4-methine protons, and no NOE was given between the isopropyl and 4-methine signals (Fig. 4b). These results strongly support the assumption that the stereochemistry of **2a** and **2b** preserves (*Z*)-configuration. Finally, the structure of **2b** was unequivocally established by X-ray crystallography as discussed below.

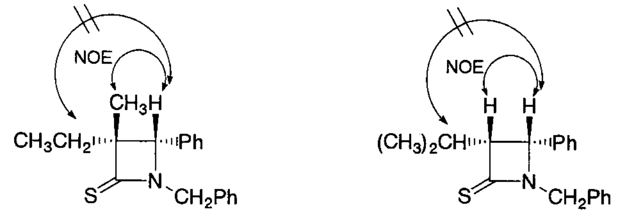
Solid-state photoreaction of 1a–1d

Fig. 2 also shows the reflective UV spectra of the crystals of thioamides **1b** and **1c**, which indicates that the molecules absorb photons sufficiently in the solid-state beyond 290 nm (Pyrex filtered light). For a practical experiment of the solid-state photoreaction, a light source from a 250 W ultra-high-pressure mercury lamp was used for the solid-state photoreactions of **1a–1d**. Single crystals placed in the bottom of a test tube were cooled to 0°C, and were irradiated by a Pyrex filtered light transmitted by quartz glass fiber from the light source.

Table 2. Photochemical reaction of **1** in benzene (a benzene solution of **1** (0.02 M) was irradiated until the starting material consumed perfectly)

1	Yield[a]	
	2	**3**
1a	56	Trace
1b	28	Trace
1c	41	31
1d	50	28

[a] Chemical yields are isolated yields.



(a) NOE for **2a** (b) NOE for **2b**

Figure 4.

As indicated by X-ray crystallographic analysis of thioamide **1a**, only the (*Z*)-isomer was obtained by thionation of the corresponding amide and crystallization process. When the solid sample of **1a** was irradiated at 0°C, the crystals gradually changed to amorphous. At this point, the generation of **2a** or **3a** was not observed (Table 3, entry 1), and only a mixture of (*E*)- and (*Z*)-isomers (*Z*/*E*=1.5) was obtained. Prolonged irradiation gave β-thiolactam **2b** in 54% yield as shown in Table 3, entry 2. The chemical yield was almost the same as that in the solution photochemistry as shown in Table 2. Namely, *E–Z* isomerization of **1a** is superior to the hydrogen abstraction in the solid-state. It appears that the solid-state photoreaction becomes dominated by the *E–Z* isomerization process because of a smaller atomic movement than that in the formation of β-thiolactam **2a**.[11] The initial step of the reaction may be interpreted in terms of an energy wasting process by *E–Z* isomerization and this creates a certain amount of free volume which may be so disposed as to allow the atomic motions required to effect a reaction, and results in disorder in the packing. It can be concluded that the *E–Z* isomerization of **1a** in the solid-state can indeed perturb the outcome of a topochemical hydrogen abstraction and the formation of **2a** in this system. According to the progression of the reaction, the crystal lattice is destroyed and the crystals would change to amorphous. In this site prolonged irradiation gave **2a** similar to the solution photochemistry.

X-Ray crystallographic analysis revealed that the crystals of

Table 3. Photochemical reaction of **1** in the solid-state

Entry	1	Conv. (%)	Yield of **2** (%)	$[\alpha]_D^{20}$ (% ee) of **2**
1	**1a**	0[a]	0	0
2		100	54	0
3	**1b**	81	55	+40(55)
4		50	60	+43(59)
5		37	71	+52(71)
6		17	95	+54(74)
7	**1c**	100	81	+94(81)
8		20	97	+112(97)
9	**1d**	100	100	0

[a] *E–Z* isomerization occurred (*Z*/*E*=1/1.5).

thioamide **1b** are chiral and the space group was $P2_12_12_1$. Fig. 3a shows the ORTEP drawing of the absolute configuration of (+)-rotatory crystals of **1b** (defined by the CD spectrum), which was determined by X-ray anomalous scattering method. This has great potential to establish the absolute asymmetric synthesis. (+)-Rotatory crystals were irradiated at 0°C until the reaction conversion reached 81% yield; it needed 2 h irradiation. As expected, the asymmetric induction in **2b** was realized by an observation of its optical rotation, which $[\alpha]_D^{20}$ value was +40° as shown in Table 3, entry 3. We tried to separate each enantiomer by HPLC with a chiral column cell; however, the available column could not be found. Finally, optically pure β-thiolactam **2b** ($[\alpha]_D^{20}=+73°$, $c=1.0$ in $CHCl_3$) was obtained by repetition of recrystallization for several times from a mixture of $CHCl_3$ and hexane. The ee value of the isolated **2b** from the solid-state photoreaction was determined as 55% ee. According to the suppression of the reaction conversion yield from 81 to 17%, the enantiomeric purity rose upto 74% ee as shown in Table 3, entries 3–6. The solution photochemistry gave an intractable mixture accompanied with 28% of **2b**. In the solid-state media, a topochemical reaction proceeded and high product selectivity was also obtained. β-thiolactam **2b** with only *Z*-configuration was isolated as in the case of solution photochemistry. We could determine the absolute configuration of (+)-**2b** as (3*S*,4*S*)-isomer by X-ray anomalous scattering method as shown in Fig. 5, which is the ORTEP drawing of (+)-**2b** obtained by the solid-state photoreaction of (+)-**1b**.

In the solid-state photoreaction of **1c**, a more chemoselective reaction occurred than that in solution, and only β-thiolactam **2c** was obtained almost quantitatively. Furthermore, the X-ray crystallographic analysis and the solid-state CD spectra revealed that the crystals of **1c** are chiral, and the space group is $P2_1$.

(+)-Rotatory (defined by the CD spectrum) crystals were used for the solid-state photoreaction. Fig. 3c shows the absolute configuration of the (+)-crystals of **1c**, which was determined by X-ray anomalous scattering method.

Of particular importance is the finding that the solid-state photoreaction of **1c** involves a crystal-to-crystal nature where the optically active β-thiolactam **2c** is formed in specific yield. Irradiation of (+)-crystals of **1c** at 0°C for 2 h exclusively gave optically active β-thiolactam **2c**, in 81% yield at 100% conversion (entry 7). As expected, the thiolactam **2c** showed optical activity ($[\alpha]_D^{20}=+94°$, 81% ee), which was determined by comparison of the $[\alpha]_D$ value with enantiomerically pure (+)-**2c** ($[\alpha]_D^{20}=+116°$, $c=1.0$ in $CHCl_3$), which was obtained by repetition of recrystallization. This reaction exhibited good enantioselectivity throughout the whole reaction, where a small difference was observed in the ee value from 97 to 81% ee with increasing conversion from 20 to 100% (Table 3, entries 7 and 8). The absolute configuration was also determined as *(R)*-configuration by X-ray anomalous scattering method as shown in Fig. 6. The solid-state photoreaction also proceeded without phase separation even after 100% reaction conversion. The crystal-to-crystal nature of the transformation was confirmed by X-ray diffraction spectroscopy.[8]

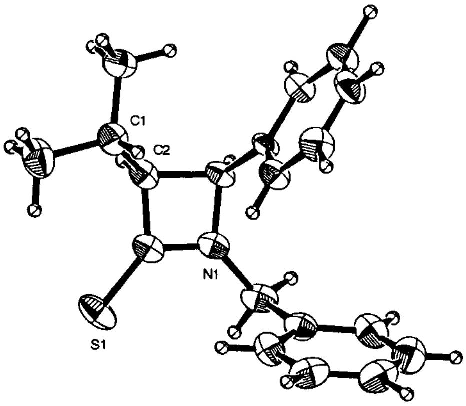


Figure 5. ORTEP drawing of the absolute configuration of (+)-**2b**.

Photolysis of cycloheptenecarbothioamide **1d** in the solid-state also gave the corresponding β-thiolactam in specific yield as shown in Table 3, entry 9. As the X-ray crystallographic analysis revealed, the crystal is racemic (Fig. 2d, Table 1), and the isolated β-thiolactam was obtained as racemate.

The geometric requirements for hydrogen abstraction and the mechanistic consideration

Fig. 7 shows the superimposed structure of each absolute structure of **1b** and **2b** established by X-ray crystallographic analysis, using an overlay program contained in CHEM3D. Since the crystals of (+)-**2b** subjected to X-ray structural analysis are recrystallized crystal, it is not possible to compare the position of atoms in detail for a phenyl ring and a benzyl group, because the chromophore can rotate freely. However, comparatively accurate information should be obtained in the rigid chromophore. These crystals maintained a solid nature in the early stage (around 50% conversion) of the photoreaction; however, phase-separation occurred in the high conversion. This phenomenon was reasonably understandable, because a drastic movement for the alkenyl group was shown in Fig. 7. The isopropylidene function and the phenyl ring of the benzyl group were placed in opposite sides of thioamide **1b**; however, each chromophore offers the same

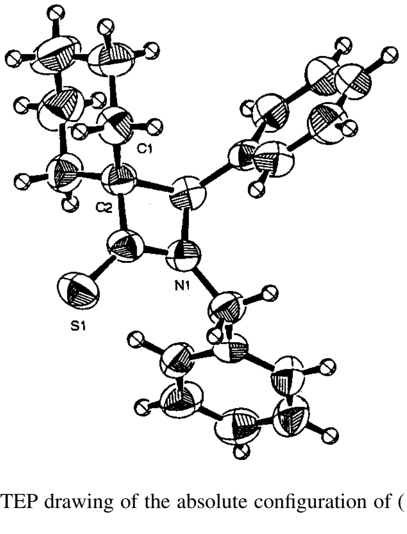


Figure 6. ORTEP drawing of the absolute configuration of (+)-**2c**.

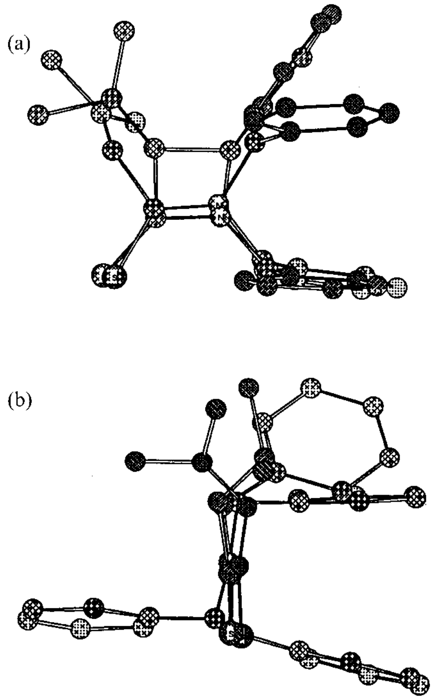


Figure 7. (a) A front view of the superimposed structure of (+)-**1b** and (+)-**2b** obtained by X-ray structural analysis using Overlay program in Chem3D. (b) The side view of the superimposed structure of (+)-**1b** and (+)-**2b**.

Z-configuration in β-thiolactam **2b**. It needs a drastic shift of the isopropylidene or phenyl group. Elucidation of each absolute configuration clearly supports that the phenyl ring is fixed in the crystal lattice, and the isopropylidene group moved to the opposite face of the thioamide plane.

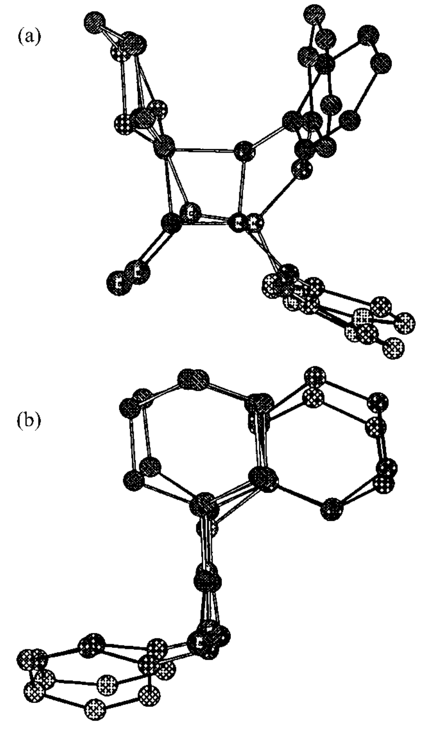


Figure 8. (a) A front view of the superimposed structure of (+)-**1c** and (+)-**2c** obtained by X-ray structural analysis using Overlay program in Chem3D. (b) The side view of the superimposed structure of (+)-**1c** and (+)-**2c**.

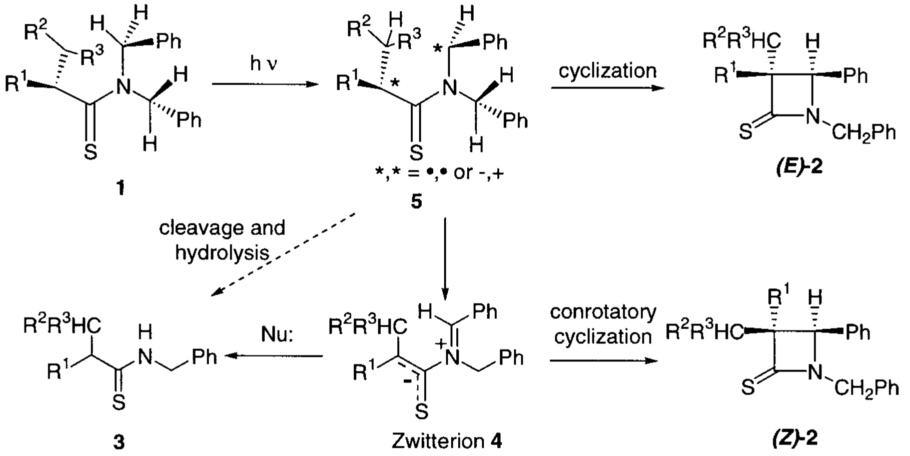
Fig. 8 is also the superimposed structure of each absolute structure of **1c** and **2c** obtained in the same manner for Fig. 7. This solid-state photoreaction maintained a crystal-to-crystal nature throughout the reaction without phase separation. Whereas the recrystallized crystals of **2c** were used for the X-ray crystallographic analysis, a really small movement of atoms was observed before and after the reaction. The maximum shift was shown in the benzyl carbon atom, where the distance was 1.24 Å. According to the cyclization the attached phenyl ring also shifted; however, the migratory distance did not exceed 1.24 Å. The cyclohexane ring went into an original space where the ring had been placed. The shift of the benzyl group, which did not participate in the hydrogen abstraction and subsequent cyclization, also did not exceed 0.65 Å. Thus, an extreme atom-shift between before and after the reaction was not needed.

We recently reported the solution photochemistry of the relevant *N*,*N*-dialkyl-α,β-unsaturated thioamides **1** leading to the β-thiolactams **2** and the debenzylated thioamide **3** initiated by hydrogen abstraction via a zwitterionic intermediate (Scheme 2).[10] Furthermore, we also reported that the solid-state photoreaction of **1c** would involve a biradical intermediate, because it may be difficult to involve a coplanar zwitterionic intermediate in the crystal lattices in the preliminary form.[8] However, a comparison of the absolute configurations of both (+)-**1b**[12] and (+)-**2b** gave us important information regarding the reaction mechanism. If the intermediate **5** was generated and the subsequent cyclization promoted, (*E*)-configuration of β-thiolactam **2b** must be obtained as shown in Scheme 3. When the reaction involves zwitterionic intermediate **4** like in a solution medium, the predominant formation of *(Z)*-**2b** is reasonably explainable by conrotatory cyclization of **4**. It is assumed that the solid-state photoreaction of **1c** and **1d** also involves a zwitterionic intermediate as in the case of **1b**, since there is no significant change in the electronic configuration due to such substituents. In conclusion, these facts indicate that the photolysis of all thioamides **1a**–**1d** gave corresponding β-thiolactams via zwitterionic intermediate **4** in both solution and the solid-state.

To investigate the relationship between the molecular conformation and the photochemical reactivity in the solid-state, all geometrical and crystallographic data required for the mechanistic analyses are collected in Table 4. With these points in mind, inspection of the geometrical data of **1** should provide further insight into the factors of lattice-controlled solid-state transformation processes.

The angle $\omega_{C=S}$ is defined as the twist angle of thiocarbonyl against the amide nitrogen, and the thioamide chromophore is almost planar as expected. On the other hand, thioamides **1** favor a conformation with the C=C double bond which is perpendicular to the thioamide chromophore in the crystal lattice, and the torsional angle is the range from 101.6 to 111.7°, then the β-alkenyl carbon is contiguous to the benzyl group.

The most important parameter is $d_{C\text{–}H}$, the distance between



Scheme 3.

the abstracted (C1) and abstracting atoms (H1) in Fig. 3. The actual distances are in the range from 2.58 to 2.68 Å, which are closely placed and within the sum of van der Waals radii 2.90 Å. The τ_{C-H} is defined as the angle formed between the C···H vector and its projection on the mean plane of the alkenyl sp^2 plane. Hydrogen abstraction is expected to be most facile when the hydrogen atom approaches the abstracting atom with maximum orbital overlap. Abstraction by a C=C carbon atom involves 2p atomic orbital which, in the ground state, is orthogonal to the double bond plane. From this geometry, the optimum value of τ_{C-H} is 90°. The last parameter is the parameter d_{C-C}, which is the distance between the atoms making a new bond. Whereas the optimum distance is anticipated within the sum of the van der Waals radii (3.4 Å), the bond formation is possible when the distance settled into 4.2 Å, which is the well-known value for 2+2 cyclobutane formation as the Schmidt rule.[13]

In this reaction, all thioamides **1a–1d** satisfy these geometrical conditions, and were offered the prominent conformation of hydrogen abstraction by alkenyl β-carbon from the benzyl group. Thioamide **1b–1d** exhibited superb photoreactivity for hydrogen abstraction; however, **1a** gave only a photostationary state of the *E–Z* isomers. Regardless of whether the conditions were satisfied for the hydrogen abstraction in the solid-state, it gave only the photostationary state of *E–Z* isomerization, because of the higher reactivity than hydrogen abstraction.

Table 4. Geometrical data for α,β-unsaturated thioamides **1a–1d**

Angle and bond length	1a	1b	1c	1d
$\omega_{C=S}$ (°)[a]	2.2	4.1	1.0	1.3
$\omega_{C=C}$ (°)[b]	101.6	111.7	110.8	100.8
d_{C-H} (Å)[c]	2.61	2.61	2.68	2.58
τ_{C-H} (°)[d]	67.3	67.3	81.2	64.5
d_{C-C} (Å)[e]	2.9	2.85	3.18	3.28

[a] The torsional angle $\omega_{C=S}$ is defined as C–N–C=S.

[b] The torsional angle $\omega_{C=C}$ is defined as S=C–C=C.

[c] d_{C-H} is the distance between the abstracted and abstracting atoms. The sum of van der Waals radii of C and H is 2.90 Å.

[d] τ_{C-H} is the angle of the C···H vector against the meaning plane of C=C double bond.

[e] d_{C-C} is the distance between two atoms making a new C–C bond. The sum of van der Waals radii of two carbon atoms is 3.40 Å.

Conclusion

The solid-state photoreaction of *N*,*N*-dibenzyl-α,β-unsaturated thioamides **1a–1d** provided a stereo- and chemoselective reaction rather than that in homogeneous conditions, and showed a different photochemical aspect owing to the substituent of the alkenyl group. The molecular conformations of the thioamides are almost the same; however, the crystal structure is different from each other. Thioamides **1b** and **1c** gave chiral crystals, and absolute asymmetric synthesis was performed by the solid-state photoreaction leading to optically active β-thiolactams. The reaction mechanism was elucidated on the basis of the relationship between the absolute configuration of the prochiral starting thioamide and the photoproducts. The solid-state photoreaction continues to present a new aspect of photochemistry and organic synthesis including absolute asymmetric synthesis.

Experimental

General

NMR spectra were recorded on $CDCl_3$ solutions on a JEOL GSX-400 and 500 operating 400 and 500 MHz, respectively, for ^1H and ^{13}C NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. Elemental analyses were made using a Perkin–Elmer 240 instrument. UV spectra were determined with a JASCO model V-570 UV/VIS/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-230 spectrometers as KBr disks, unless otherwise noted. Optical rotations were determined on a JASCO DIP-370 polarimeter operating at the sodium D line in $CHCl_3$ solution at the concentration of c=1.0.

General procedure for the preparation of *N*,*N*-dibenzyl-α,β-unsaturated thioamides (1a–1d)

All α,β-unsaturated thioamides **1a–1d** were prepared by sulfurization of the corresponding α,β-unsaturated amides with diphosphorus pentasulfide or Lawesson's reagent. The requisite α,β-unsaturated amides can be easily prepared by the condensation of the corresponding acid chlorides and amines in the presence of triethylamine. A synthesis of **1a** was exemplified as follows. To a toluene solution containing 2.95 g (10 mmol) of the *N*,*N*-dibenzyltiglylamide was added 1.1 g (5.5 mmol) of Lawesson's reagent at room temperature. The reaction mixture was heated at 80°C with stirring for 3 h and then cooled to room temperature and filtered on Celite column. The filtrate was subjected to chromatography on silica gel and the crystalline thioamide **1a** was recrystallized from $CHCl_3$–hexane; afforded slightly yellow crystals. The structure of **1a**–**1d** was determined on the basis of spectral data, elemental analysis, mass spectroscopy, and unequivocally X-ray crystallographic analyses.

(*Z*)-*N*,*N*-Dibenzyltiglylthioamide 1a was obtained as slightly yellowish prismatic crystals from hexane–chloroform: yield 68%; mp 72–73°C; IR (cm^{-1}, KBr) 1193, 1451, 1469; UV (nm, in C_6H_{12}) 287 (ϵ 13300), 336 (ϵ 430); ^{1}H NMR ($CDCl_3$) δ 1.65 (d, *J*=7.0 Hz, 3H, *Me*CH=C), 2.05 (s, 3H, CH=C*Me*) 4.50 and 4.92 (ABq, *J*=15.2 Hz, 2H, C*H*$_2$Ph), 4.77 and 5.79 (ABq, *J*=15.2 Hz, 2H, C*H*$_2$Ph), 5.27 (q, *J*=7.0 Hz, 1H, MeC*H*=C), 7.1–7.4 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 15.0 (q, *Me*CH=C), 23.4 (q, CH=C*Me*), 52.1 (t, *C*H$_2$Ph), 54.2 (t, *C*H$_2$Ph), 120.8 (d, Me*C*H=C), 127.7 (d, Ar), 128.2 (d, Ar), 128.3 (d, Ar), 128.8 (d, Ar), 129.0 (d, Ar), 129.3 (d, Ar), 135.3 (s, Ar), 135.8 (s, Ar), 139.0 (s, MeCH=*C*), 204.9 (s, C=S). Anal. Calcd for $C_{19}H_{21}NS$: C, 77.24%; H, 7.16%; N, 4.74%. Found: C, 77.26%; H, 7.10%; N, 4.69%.

***N*,*N*-Dibenzyl-1-methylcrotonthioamide 1b** was obtained as yellow prismatic crystals from hexane–chloroform: yield 60%; mp 64–65°C; IR (cm^{-1}, KBr) 1168, 1227, 1426, 1469; UV (nm, in C_6H_{12}) 292 (ϵ 11300), 398 (310); ^{1}H NMR ($CDCl_3$) δ 1.79 (d, *J*=1.1 Hz, 3H, *Me*$_2$C=CH), 1.82 (d, *J*=1.1 Hz, 3H, *Me*$_2$C=CH), 4.74 (s, 2H, C*H*$_2$Ph), 5.27 (s, 2H, C*H*$_2$Ph), 6.1 (s, 1H, Me$_2$C=C*H*), 7.11 (m, 2H, ArH), 7.3–7.4 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) δ 19.8 (q, *Me*$_2$C=CH), 25.4 (q, *Me*$_2$C=CH), 52.8 (t, *C*H$_2$Ph), 54.1 (t, *C*H$_2$Ph), 125.8 (d, Ar), 127.0 (d, Ar), 127.8 (d, Ar), 128.0 (d, Ar), 128.3 (d, Ar), 128.7 (d, Me$_2$C=*C*H), 129.0 (d, Ar), 135.1 (s, Ar), 135.7 (s, Me$_2$*C*=CH), 138.0 (s, Ar), 200.1 (s, C=S). Anal. Calcd for $C_{19}H_{21}NS$: C, 77.24%; H, 7.16%; N, 4.74%. Found: C, 77.12%; H, 7.01%; N, 4.73%.

***N*,*N*-Dibenzyl-1-cyclohexenecarbothioamide 1c** was obtained as slightly yellow prismatic crystals from hexane–chloroform: yield 75%; mp 73–74°C; IR (cm^{-1}, KBr) 1495; UV (nm, in C_6H_{12}) 240 (ϵ 13800), 289 (ϵ 13700); ^{1}H NMR ($CDCl_3$) δ 1.5–1.7 (m, 6H, (C*H*$_2$)$_3$), 2.0–2.2 (m, 2H, C*H*$_2$), 4.74 (s, 2H, C*H*$_2$Ph), 5.25 (brs, 2H, C*H*$_2$Ph), 5.75 (m, 1H, C*H*=C), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$): δ 21.4 (t, *C*H$_2$), 22.3 (t, *C*H$_2$), 24.5 (t, *C*H$_2$), 28.5 (t, *C*H$_2$), 52.3 (t, *C*H$_2$Ph), 54.5 (t, *C*H$_2$Ph), 123.8 (s, CH=*C*), 127.2 (d, *C*H=C), 127.7 (d, Ar), 127.9 (d, Ar), 128.0 (d, Ar), 128.7 (d, Ar), 129.0 (d, Ar), 135.4 (s, Ar), 141.2 (s, Ar), 206.2 (s, C=S). Anal. Calcd for $C_{21}H_{23}NS$: C, 78.46%; H, 7.21%; N, 4.36%. Found: C, 78.56%; H, 7.25%; N, 4.35%.

***N*,*N*-Dibenzyl-1-cycloheptenenecarbothioamide 1d** was obtained as yellow prismatic crystals from hexane–chloroform: yield 70%; mp 82.5–84.0°C; IR (cm^{-1}, KBr) 1495; UV (nm, in C_6H_{12}) 290 (ϵ 12000); ^{1}H NMR ($CDCl_3$) δ 1.5–1.7 (m, 6H, (C*H*$_2$)$_4$), 2.1–2.2 (m, 2H, C*H*$_2$), 2.3–2.7 (m, 2H, C*H*$_2$), 4.77 (brs, 2H, C*H*$_2$Ph), 5.23 (s, 2H, C*H*$_2$Ph), 5.88 (m, 1H, C*H*=C), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$): δ 26.2 (t, *C*H$_2$), 27.1 (t, *C*H$_2$), 28.4 (t, *C*H$_2$), 31.6 (t, *C*H$_2$), 33.5 (t, *C*H$_2$), 51.9 (t, *C*H$_2$Ph), 54.5 (t, *C*H$_2$Ph), 127.0 (s, CH=*C*), 127.5 (d, *C*H=C), 127.8 (d, Ar), 128.6 (d, Ar), 128.8 (d, Ar), 135.3 (s, Ar), 146.1 (s, Ar), 207.2 (s, C=S). Anal. Calcd for $C_{22}H_{25}NS$: C, 78.76%; H, 7.51%; N, 4.17%. Found: C, 78.77%; H, 7.69%; N, 4.06%.

X-Ray crystallographic analysis of (*Z*)-*N*,*N*-dibenzyltiglylthioamide 1a. Slightly yellow prismatic crystals from hexane–chloroform, monoclinic space group $P2_1/a$, a=17.430 (4) Å, b=15.382 (4) Å, c=6.557 (2) Å, β=99.64° (2), V=1733.1 (8) Å^3, Z=4, ρ=1.13 g/cm^3, $\mu(CuK_\alpha)$=15.48 cm^{-1}. The structure was solved by the direct method and refined by the method of full-matrix least-squares, where the final R and R_w were 0.043 and 0.046 for 2673 reflections.

X-Ray crystallographic analysis of (+)-(*Z*)-*N*,*N*-dibenzyl-3-methylcrotonthioamide 1b. (+)-Rotatory crystal was subjected to X-ray crystallography, yellow prismatic crystals from hexane–chloroform, orthorhombic space group $P2_12_12_1$, a=13.232(6) Å, b=17.928(6) Å, c=7.125(6) Å, V=1690(1) Å^3, Z=4, ρ=1.16 g/cm^3, $\mu(CuK_\alpha)$= 16.24 cm^{-1}. The absolute structure of (+)-**1b** was solved by the Bijvoet difference method. A total of 2200 Friedel pairs with F_c differing significantly at the end of the refinement were measured with great care. For these, 428 agreement and 235 disagreement between the observed and calculated *DF* for the structure with a configuration for the helix as shown in Fig. 2b gives clear evidence that this structure has the correct absolute configuration, where the final R and R_w were 0.055 and 0.062.

X-Ray crystallographic analysis of (+)-*N*,*N*-dibenzyl-1-cyclohexenecarbothioamide 1c. (+)-Rotatory crystal was subjected to X-ray crystallography, slightly yellow prismatic crystals from hexane–chloroform, monoclinic space group $P2_1$, a=8.760 (2) Å, b=10.262 (3) Å, c=10.238 (3) Å, b=100.15 (2)°, V=905.9 (4) Å^3, Z=2, ρ=1.178 g/cm^3, $\mu(CuK_\alpha)$=15.55 cm^{-1}. The absolute structure of (+)-**1c** was solved by the Bijvoet difference method. A total of 962 Friedel pairs with F_c differing significantly at the end of the refinement were measured with great care. For these, 669 agreement and 293 disagreement between the observed and calculated *DF* for the structure with a configuration for the helix as shown in Fig. 2c gives clear evidence that this structure has the correct absolute configuration, where the final R and R_w were 0.063 and 0.057.

X-Ray crystallographic analysis of *N*,*N*-dibenzyl-1-cycloheptenecarbothioamide 1d. Slightly yellow prismatic crystals from hexane–chloroform, monoclinic space group $P2_1/n$, a=7.205 (10) Å, b=11.81 (2) Å, c=22.57 (3) Å, β=92.13 (9)°, V=1919 (4) Å^3, Z=4, ρ=1.178 g/cm^3, $\mu(MoK_\alpha)$=1.71 cm^{-1}. The structure was solved by the direct method and refined by the method of full-matrix least-squares, where the final R and R_w were 0.097 and 0.133 for 2489 reflections.

General procedure for the photochemical reaction in benzene

A benzene solution of thioamide **1a–1d** (0.02 M) was purged with deoxygenated and dried argon for 15 min prior to photolysis and was irradiated with a 500 W Eikosha high-pressure mercury lamp through a Pyrex filter. After irradiation, benzene was evaporated and the photolysate was chromatographed on silica gel (Merk Kieseigel 60) with ethyl acetate–hexane (10:1) as the eluent.

General procedure for the photochemical reaction in the solid-state

All of the solid-state photolyses were done under an atmosphere of deoxygenated and dried argon. Solid samples placed in the test tube were cooled in a cooling apparatus, and were irradiated with a 500 W high-pressure mercury lamp. After irradiation, the photolysate was treated the same as that in solution photochemistry.

(*E*)-*N*,*N*-Dibenzyltiglylthioamide (*E*)-1a was analyzed for ^{1}H and ^{13}C NMR spectroscopy as a crude reaction mixture: ^{1}H NMR ($CDCl_3$) δ 1.68 (d, J=6.8 Hz, 3H, *Me*CH=C), 1.99 (s, 3H, CH=C*Me*), 4.71 (s, 2H, C*H*$_2$Ph), 5.25 (s, 2H, C*H*$_2$Ph), 5.58 (dq, J=1.5 and 7.0 Hz, 1H, MeC*H*=C), 7.1–7.4 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 13.4 (q, *Me*CH=C), 16.5 (q, CH=C*Me*), 52.3 (t, *C*H$_2$Ph), 54.6 (t, *C*H$_2$Ph), 122.1 (d, Me*C*H=C), 127.2 (d, Ar), 127.4 (d, Ar), 127.9 (d, Ar), 128.0 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 135.0 (s, Ar), 135.3 (s, Ar), 138.7 (s, MeCH=*C*), 207.1 (s, C=S).

(*Z*)-1-Benzyl-3-ethyl-3-methyl-4-phenylazetidine-2-thione 2a was obtained as colorless prismatic crystals from hexane–chloroform: mp 61–62°C; IR (cm^{-1}, KBr) 1496; UV (nm, in C_6H_{12}) 268 (ϵ 15800); ^{1}H NMR ($CDCl_3$) δ 0.56 (t, J=7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.25 (m, 1H, C*H*$_2$CH$_3$), 1.34 (s, 3H, C(Et)*Me*), 1.53 (m, 1H, C*H*$_2$CH$_3$), 4.03 and 5.44 (ABq, J=14.3 Hz, 2H, C*H*$_2$Ph), 4.60 (s, 1H, C*H*Ph), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 7.7 (q, CH$_2$*C*H$_3$), 16.8 (q, C(Et)*Me*), 25.3 (t, *C*H$_2$CH$_3$), 46.2 (t, *C*H$_2$Ph), 60.2 (s, *C*(Et)Me), 73.8 (s, *C*HPh), 128.4 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 134.3 (s, Ar), 134.5 (s, Ar), 211.3 (s, C=S); LRMS (FAB) Calcd for $C_{20}H_{30}NS_2$: *m*/*z* 296.

(3*S*,4*S*)-1-Benzyl-3-isopropyl-4-phenylazetidine-2-thione 2b was obtained as colorless prismatic crystals: mp 94–95°C; $[\alpha]_D^{20}=+73°$, c=1.0 in $CHCl_3$); IR (cm^{-1}, KBr) 1496; UV (nm, C_6H_{12}) 243 (ϵ 9600), 274 (ϵ 15600); ^{1}H NMR ($CDCl_3$) δ 0.35 (d, 3H, J=6.6 Hz, CH*Me*$_2$), 1.30 (d, 3H, J=6.6 Hz, CH*Me*$_2$), 1.80 (m, 1H, C*H*Me$_2$), 3.02 (dd, 1H, J=4.7 and 11.5 Hz, C*H*Pr^i), 3.96 and 5.37 (ABq, 2H, J=14.4 Hz, C*H*$_2$Ph), 4.99 (d, 1H, J=4.6 Hz, C*H*Ph), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 20.3 (q, CH*M*$_{e2}$), 26.7 (d, *C*HMe$_2$), 46.4 (d, *C*HPr^i), 65.7 (t, *C*H$_2$Ph), 67.9 (s, *C*HPh), 127.9 (d, Ar), 128.0 (d, Ar), 128.2 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 134.0 (s, Ar), 134.3 (s, Ar), 204.9 (s, C=S). Anal. Calcd for $C_{19}H_{21}NS$: C, 77.24%; H, 7.16%; N, 4.74%. Found: C, 77.26%; H, 7.24%; N, 4.77%.

The absolute configuration was determined by X-ray crystallographic analysis: monoclinic space group $P2_12_12_1$, a=8.8350 (9) Å, b=30.294 (5) Å, c=6.295 (2) Å, V=1684.9 (6) Å^3, Z=4, ρ=1.165 g/cm^3, μ(CuK$_\alpha$)=16.29 cm^{-1}. The structure was solved by the direct method and refined by the method of full-matrix least-squares. The absolute configuration was solved by the Bijvoet difference method. For 2223 Friedel pairs, 438 agreement and 241 disagreement between observed and calculated *DF* for the structure with the (3*S*,4*S*)-configuration clearly showed that this structure is that with the correct absolute configuration, where the final R and R_w were 0.055 and 0.064 for 3678 reflections.

(*R*)-1-Benzyl-4-phenylazetidine-2-thione-3-spiro-1′-cyclohexane 2c was obtained as colorless prismatic crystals from hexane–chloroform: mp 109–110°C; $[\alpha]_D^{20}=+116°$ (c=1.0 in $CHCl_3$); IR (cm^{-1}, KBr) 1495; UV (nm, C_6H_{12}) 269 (ϵ 16200); ^{1}H NMR ($CDCl_3$) δ 0.5–0.7 (m, 1H, C*H*$_2$), 1.2–1.7 (m, 7H, C*H*$_2$), 1.8–2.0 (m, 2H, C*H*$_2$), 3.99 and 5.43 (ABq, 2H, J=14.5 Hz, C*H*$_2$Ph), 4.63 (s, 1H, 4-C*H*), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4 (t, CH$_2$), 23.1 (t, CH$_2$), 24.8 (t, CH$_2$), 27.8 (t, CH$_2$), 34.3 (t, CH$_2$), 44.1 (t, *C*H$_2$Ph), 61.5 (s, 3-C), 73.8 (d, 4-C), 127.5 (d, Ar), 128.0 (d, Ar), 128.5 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 134.2 (s, Ar), 134.6 (s, Ar), 210.8 (s, C=S); LRMS (FAB) Calcd for $C_{20}H_{30}NS_2$: *m*/*z* 322. Anal. Calcd for $C_{21}H_{23}NS$: C, 78.46%; H, 7.21%; N, 4.36%. Found: C, 78.66%; H, 7.39%; N, 4.34%.

The absolute configuration was determined by X-ray crystallographic analysis: monoclinic space group $P4_3$, a=10.366 (1) Å, c=17.133 (3) Å, V=1841.0 (4) Å^3, Z=4, ρ=1.160 g/cm^3, μ(CuK$_\alpha$)=15.30 cm^{-1}. The structure was solved by the direct method and refined by the method of full-matrix least-squares. The absolute configuration was solved by the Bijvoet difference method. For 2391 Friedel pairs, 675 agreement and 351 disagreement between observed and calculated *DF* for the structure with the *(R)*-configuration clearly showed that this structure is that with the correct absolute configuration, where the final R and R_w were 0.052 and 0.071 for 3226 reflections.

1-Benzyl-4-phenylazetidine-2-thione-3-spiro-1′-cycloheptane 2d was obtained as colorless prismatic crystals from hexane–chloroform: mp 92–92.5°C; IR (cm^{-1}, KBr) 1495; UV (nm, in C_6H_{12}) 239 (ϵ 10300), 268 (ϵ 16000); ^{1}H NMR ($CDCl_3$) δ 0.9–1.1 (m, 1H, C*H*$_2$), 1.2–1.9 (m, 8H, C*H*$_2$), 2.0–2.1 (m, 1H, C*H*$_2$), 3.99 and 5.43 (ABq, 2H, J=14.5 Hz, C*H*$_2$Ph), 4.64 (s, 1H, 4-C*H*), 7.1–7.4 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 23.2 (t, CH$_2$), 24.1 (t, CH$_2$), 29.7 (t, CH$_2$), 29.8 (t, CH$_2$), 31.8 (t, CH$_2$), 37.0 (t, CH$_2$), 46.7 (t, *C*H$_2$Ph), 64.3 (s, 3-C), 75.0 (d, 4-C), 127.8 (d, Ar), 128.4 (d, Ar), 128.8 (d, Ar), 129.1 (d, Ar), 129.2 (d, Ar), 134.9 (s, Ar), 135.0 (s, Ar), 212.7 (s, C=S); Anal. Calcd for $C_{21}H_{23}NS$: C, 78.76%; H, 7.51%; N, 4.17%. Found: C, 78.63 %; H, 7.56 %; N, 4.02 %.

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