Cyclization of Hindered Fluorinated Dichloro(5- and 6-)alkenyl Radicals. Structural Effects of Olefins on the Selective Formation of 5-*exo* and 6-*endo* Cyclization Products

Takashi Okano, Hidemasa Ishihara, Nobuyuki Takakura, Hiroyasu Tsuge, Shoji Eguchi,* and Hiroshi Kimoto†

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464−01, Japan, and National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan

Received April 9, 1997[⊗]

Reaction of 3-butenyl radicals generated by photolysis of variously substituted Barton esters (both open-chain **1a**−**d** and cyclohexyl **1e**−**h**) with CF_2=CCl_2 gave a mixture of cyclized products (cyclopentanes **6** and **8** and cyclohexanes **7** and **9**) as well as noncyclized products (**4** and **5**) in various ratios depending on the substitution pattern at the olefinic moiety. The product ratios of [cyclization (**6** + **7** + **8** + **9**):noncyclization (**5**)] for **1** with more alkyl substituents on the CC double bond were greater than those for **1** with fewer substituents. The products ratio of [5-*exo* (**6** + **8**): 6-*endo* (**7** + **9**)] was influenced by a steric effect. Photoreaction of Barton ester **2** with CF_2=CCl_2 gave a mixture of cyclohexanes **16** and **17** as well as noncyclized **14** and **15**. Dehydrochlorination of decalins **7g** and **7h** followed by oxidation of sulfide and [2,3]sigmatropic rearrangement of the allyl sulfoxide gave octahydronaphthalenones **23** and **27**, respectively.

The C−C bond-forming reactions via carbon radical intermediates are currently some of the most important methods in the organic syntheses.[1] In particular, radical cyclization has been intensively investigated and applied to the construction of complex carbocycles, and preferential 5-*exo* cyclization has been established for the cyclization of 5-hexenyl radicals.[2] In the case of some stable and hindered 5-hexenyl radicals, the selectivity changes to 6-*endo* cyclization.[3]

Recently, we developed an alkyl radical addition pathway to obtain α,α-difluorocarboxylic acids and their esters via addition of alkyl radicals generated by the photolysis of thiohydroxamic carboxylic mixed anhydrides (Barton esters)[4] in the presence of CF_2=CCl_2 followed by hydrolysis or methanolysis with $AgNO_3$.[5] Among the various Barton esters used, we obtained a complex mixture of radical products from Barton ester of 5-pentenoic acid (**1a**). This result was due to contamination by cyclized products accompanying the major noncyclized radical addition products, and 6-membered-ring products were obtained in this reaction as well as the usual 5-membered products. We were interested in the formation of these unusual 6-membered products and also in the value of this radical cyclization for the synthesis of a new class of fluorinated cyclic compounds.[6,7] We report here the relationship between the structure of the olefin moiety of the initially generated 3-butenyl radical and cyclization selectivity. We also converted the products of selective cyclization into difluorooctahydronaphthalones.

Results and Discussion

Barton esters **1a**−**h** and **2** (Chart 1) were obtained by standard condensation procedures from the corresponding alkenecarboxylic acids and *N*-hydroxypyridinethione with dicyclohexylcarbodiimide in yields of 70−98%.[4,5] Photoreactions of Barton esters **1a**−**h** and **2** were conducted as described previously:[5] a mixture of the Barton ester and a 10-molar amount of CF_2=CCl_2 (**3**) in CH_2Cl_2 was irradiated with a 500-W tungsten lamp, and the

† National Industrial Research Institute of Nagoya.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

(1) (a) Motherwell. W. B.; Crich. D. *Best Synthetic Methods, Free Radical Chain Reactions in Organic Synthesis*; Academic Press: London, 1992. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (d) Curran, D. P. *Synthesis* **1988**, 417 and 489. (e) Jasperse, C. P.; Curran, D. P. *Chem. Rev.* **1991**, *91*, 1237. (f) Curran, D. P. *Synlett* **1991**, 63. (g) Malacria, M. *Chem. Rev.* **1996**, *96*, 289.

(2) (a) Giese, B.; Kopping, B.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. *Org. Reactions* **1996**, *48*, 301. (b) Surzur, J.-M. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; Vol. 2, pp 121. (c) Beckwith, A. L.; Ingold, K. U. *Rearrangements in Ground and Exited States*; de Mayo, P., Ed.; Academic Press, New York, 1980; Vol. 1, pp 161.

(3) (a) Schultz, A. G.; Guzzo, P. R.; Nowak, D. M. *J. Org. Chem.* **1995**, *60*, 8044. (b) Clive, D. L. J.; Tao, Y.; Khodabocus, A.; Wu, Y-J.; Angoh, A. G.; Bennet, S.; Boddy, C.; Bordeleau, L.; Kellner, D.; Kleiner, G.; Middleton, D. S.; Nichols, C.; Richardson, S.; Vernon, P. G. *J. Am. Chem. Soc.* **1994**, *116*, 11275. (c) Schultz, A. G.; Holoboski, M. A.; Smyth, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 7904. (d) Srikrishna, A.; Sundarababu, G. *Tetrahedron Lett.* **1991**, *47*, 481. (e) Bailey, W. F.; Khanolkar, A. D. *Tetrahedron Lett.* **1991**, *47*, 7727. (f) Ward, J. E.; Keller, B. F. *Tetrahedron Lett.* **1991**, *32*, 843. (g) Takano, S.; Suzuki, M.; Kijima, A.; Ogasawara, K. *Tetrahedron Lett.* **1990**, *31*, 2315. (h) Curran, D.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. (i) Morikawa, T.; Nishiwaki, T.; Kobayashi, K. *Tetrahedron Lett.* **1989**, *30*, 2407. (j) Urabe, H.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 1355.

(4) Crich, D. *Aldrichimica Acta* **1987**, *20*, 35. Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.* **1986**, *58*, 675. Barton, D. H. R.; Samadi, M. *Tetrahedron* **1992**, *48*, 7083. Barton, D. H. R.; Herv, Y.; Potier, P.; Thierry, J. *Tetrahedron* **1987**, *43*, 6127. Barton, D. H. R; Ozbalik, N.; Vacher, B. *Tetrahedron* **1988**, *44*, 3501.

(5) Okano, T.; Takakura, N.; Nakano, Y; Okajima, A. Eguchi, S. *Tetrahedron* **1995**, *51*, 1903. Okano, T.; Takakura, N.; Nakano, Y.; Eguchi S. *Tetrahedron Lett.* **1992**, *33*, 3491.

(6) For the recent review of synthesis of difluoromethylene compounds, see: Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 232. For the reviews of biological activities of fluorinated compounds, see: Welch, J. T. *Selective Fluorination in Organic and Bioorganic Chemistry*; ACS Symposium Series 456; American Chemical Society: Washington, DC, 1991. Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; John Wiley & Sons: New York, 1990. Welch, J. T. *Tetrahedron* **1987**, *16*, 381.

(7) Some examples of radical cyclization reactions of difluoromethylene-containing alkenyl radicals leading to 5-*exo* cyclization were reported: (a) Arnone, A.; Bravo, P.; Caviccho, M.; Frigerio, M.; Viani, F. *Tetrahedron* **1992**, *48*, 8523. (b) Morikawa, T.; Kodama, Y.; Uchida, J.; Takano, M.; Washio, Y.; Taguchi, T. *Tetrahedron* **1992**, *48*, 8915. (c) Arnone, A.; Bravo, P.; Viani, F. *Tetrahedron Asymmetry* **1992**, *2*, 399. (d) Barth, F.; O-Yang, C. *Tetrahedron Lett.* **1991**, *32*, 5873.

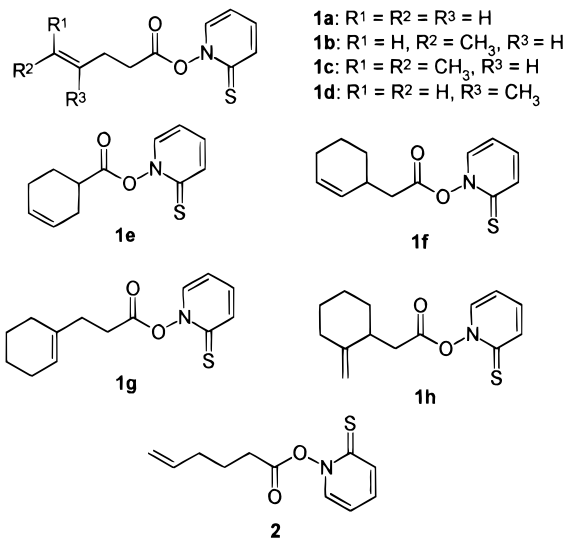
S0022-3263(97)00639-7 CCC: $14.00

Table 1. Photoreaction of Barton Esters 1a−h with Olefin 3

entry	Barton ester	products (% yield)[a]	product ratios: cyclic/acyclic [(**6** + **7** + **8** +**9**)/**5**]	product ratios: 5-membered/6-membered [(**6** + **8**)/(**7** + **9**)]
1	**1a**	**4a** (26), **5a** (35), **6a** (13), **7a** (4), **8a** (8), **9a** (4)	45/55	72/28
2	**1b**	**4b** (11), **5b** (5), **6b*e*** (34), **6b*t*** (6), **7b** (8), **8b** (7), **9b** (7)	93/7	76/24
3	**1c**	**4c** (19), **5c** (trace), **6c** (53), **8c** (6)	>99/1	>99/1
4	**1d**	**4d** (19), **5d** (22), **7d** (38), **9a** (10)	69/32	<1/99
5	**1e**	**4e** (13), **5e** (68)	<1/99	
6	**1f**	**4f** (18), **5f** (14), **6f** (25), **8f** (23)	77/23	>99/1
7	**1g**	**4g** (23), **5g** (8), **7g** (54)[b]	87/13	<1/99
8	**1h**	**4h** (14), **5h** (7), **7h** (52)	88/12	<1/99

[a] Yields are isolated ones except for the yields of the combinations of **8a** and **9a**, **8b** and **9b**, and **5g**, which were roughly estimated from the obtained amounts of the mixtures based on the ^{1}H NMR spectra (**8b** and **9b**, and **5g**) or the ^{13}C NMR spectrum (**8a** and **9a**). See the Experimental Section. [b] 86:14 mixture of *cis*/*trans* products.

Chart 1



products were separated by silica gel chromatography. Some of the cyclization products were inseparable, and their structures were assigned by their ^{1}H- and ^{13}C-NMR spectra.

The analyzed products of the reaction of **1a** and **3** are the self-trapping product of the butenyl radical (**4a**, 26%), the uncyclized addition product (**5a**, 35%), cyclopentane (**6a**, 13%), cyclohexane (**7a**, 4%), and an inseparable mixture of **8a** and **9a** (12%; **8a**:**9a** = 2:1). The structures of **4a** and **5a** were readily determined by their ^{1}H- and ^{13}C-NMR spectra, in which signals of the butenyl group were observed, indicating no cyclization. In the ^{1}H-NMR spectrum of **6a**, a pair of doublet-of-doublets peaks in the lower field revealed the existence of an exocyclic CH_2SPy group in the cyclopentane structure of **6a**. Similarly, the cyclohexane structure of **7a** was determined by its ^{1}H-NMR spectrum, in which a triplet-of-triplets (J = 13 and 4 Hz) in the lower field reflected the usual axial−axial and axial−equatorial proton couplings of cyclohexane. GC−MS analysis and elemental analysis of the mixture of **8a** and **9a** supported the notion that both components have the formula $C_{13}H_{11}Cl_4F_4NS$. On the basis of the similarity of this ^{1}H-NMR spectrum to those of **6a** and **7a**, these were determined to be cyclized 1:2 adducts. The reaction is summarized in Scheme 1. Photolytically generated butenyl radical **10a** reacts with **3**, to form an intermediate dichloroalkyl radical **11a**, and with **1a**, to give self-trapping product **4a**. The electron-deficient radical **11a** gives adduct **5a** without cyclization and secondary intermediates **12a** and **13a** after cyclization. Trapping of **12a** or **13a** with **1a** affords cyclized 1:1 adducts **6a** or **7a**, respectively. However, since cyclized radicals **12a** and **13a** are again nucleophilic radicals, trapping with **3** occurs to yield the cyclized 1:2 adducts **8a** and **9a**, respectively.

The products from Barton esters **1b**−**h** are summarized in Charts 2 and 3 and Table 1. The structures of the products were determined as with the products from **1a**. In Table 1, the yields of the products and the ratios of cyclic and acyclic products and 5- and 6-membered products are summarized. Although methyl substitution at the end of the CC double bond (entry 2) has little effect on cyclopentane/cyclohexane selectivity [from 72 (**6a** + **8a**):28 (**7a** + **9a**) to 76 (**6b** + **8b**):24 (**7b**+ **9b**)], the relative yield of cyclic products increased from 45 (**6a** + **7a** + **8a** + **9a**):55 (**5a**) to 93 (**6b** + **7b** + **8b** + **9b**):7 (**5b**) with an increase in the electron density of the CC double bond. The stereochemistry of **6b*t*** and **6b*e*** was determined by the ^{1}H-NMR coupling constants $J_{H^{1'}-H^3}$ = 11 Hz as a *trans*-coupling for *erythro*-**6b*e***, and $J_{H^{1'}-H^3}$ = 7 Hz, as *gauche*-coupling for *threo*-**6b*t***, respectively. Similarly, the *trans*-stereochemistry of **7b** was determined by the ^{1}H-NMR coupling constant ($J_{H^3-H^4}$ = 12 Hz), which indicated axial−axial coupling. Although 1:2 adducts **8b** and **9b** were obtained as a mixture, a similar analysis of the ^{1}H-NMR spectrum suggested the same stereoselectivity. The diastereoselective formation of **6b**−**9b** in the acyclic radical reaction system for **6b*e*** and **8b** and in the substituted cyclohexyl radicals for **7b** and **9b** is in accordance with the previously reported selective formation of radical products.[8,9] The preferential cyclization was enhanced by substitution of another methyl group on the CC double bond, and nearly complete cyclization was observed in the reaction of **1c**. Furthermore, a steric effect prevents the unfavorable 6-*endo* cyclization to cyclohexane derivatives, and 5-membered products **6c** and **8c** were obtained selectively. As shown above, the cyclization of dichloroalkenyl radical intermediates occurs at the less-substituted carbon of the π-bond. In the case of **1d**, since the terminal carbon is unhindered, the resulting cyclization products are cyclohexanes

(8) Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296. Giese, B.; Carboni, B.; Göbel, T.; Muhn, R.; Wetterich, F. *Tetrahedron Lett.* **1992**, *33*, 2673. Giese, B.; Damm, W.; Wetterich, F.; Zeitz, H.-G. *Tetrahedron Lett.* **1992**, *33*, 1863. Tanabe, Y.; Wakimura, K.; Nishii, Y. *Tetrahedron Lett.* **1996**, *37*, 1837. Hassler, C.; Batra, R.; Giese, B. *Tetrahedron Lett.* **1995**, *36*, 7639. Guidon, Y.; Yoakin, C; Lemieux, R.; Boisvert, L.; Delorme, K.; Lavallée, J.-F. *Tetrahedron Lett.* **1990**, *31*, 2845. Durkin, K.; Liotta, D.; Rancourt, J.; Lavalllée, J.-F.; Boisvert, L.; Guidon, Y. *J. Am. Chem. Soc.* **1992**, *114*, 4912. Kündig, E. P.; Xu, L.-H.; Romanens, P. *Tetrahedron Lett.* **1995**, *36*, 4047. Curran, D. P.; Geib, S. J.; Kuo, L. H. *Tetrahedron Lett.* **1994**, *35*, 6235.

(9) Damm, W.; Giese, B.; Hartung, J.; Hasskerl, T.; Houk, K. N.; Hueter, O.; Zipse, H. *J. Am. Chem. Soc.* **1992**, *114*, 4067. Giese, B. Angew. *Chem., Int. Ed., Engl.* **1989**, *28*, 969.

Scheme 1

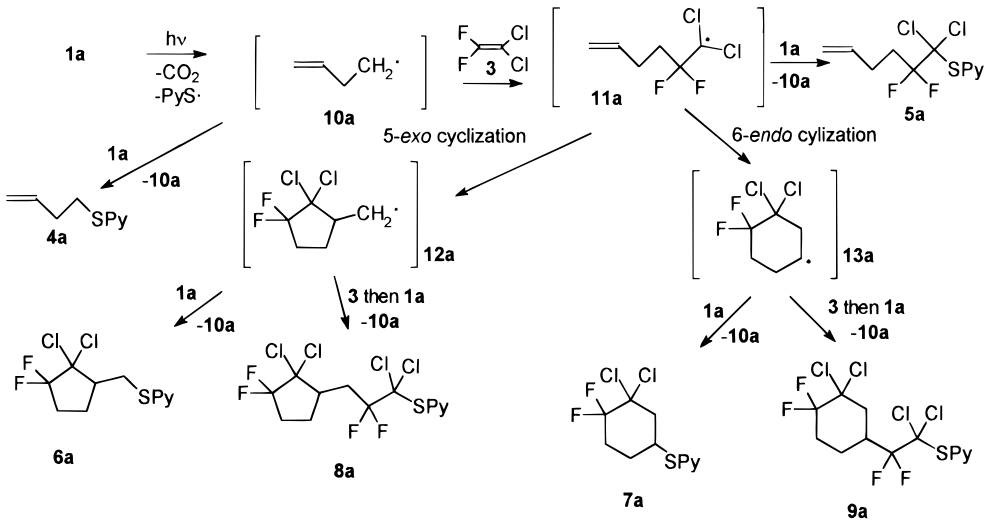


Chart 2

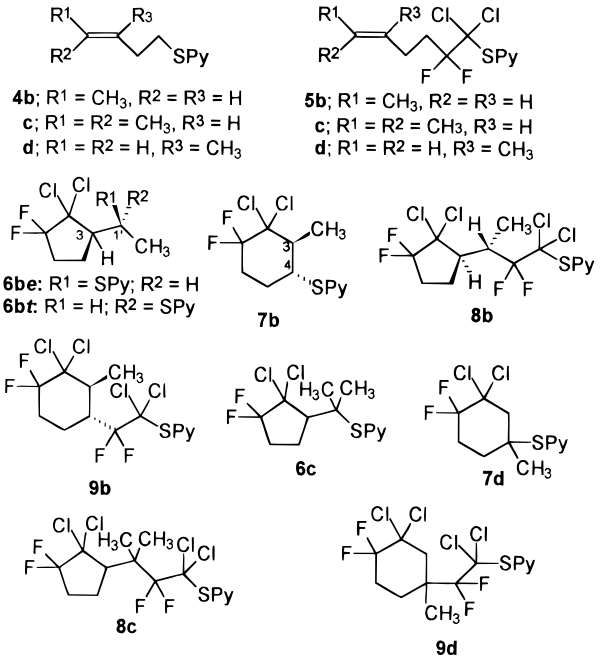
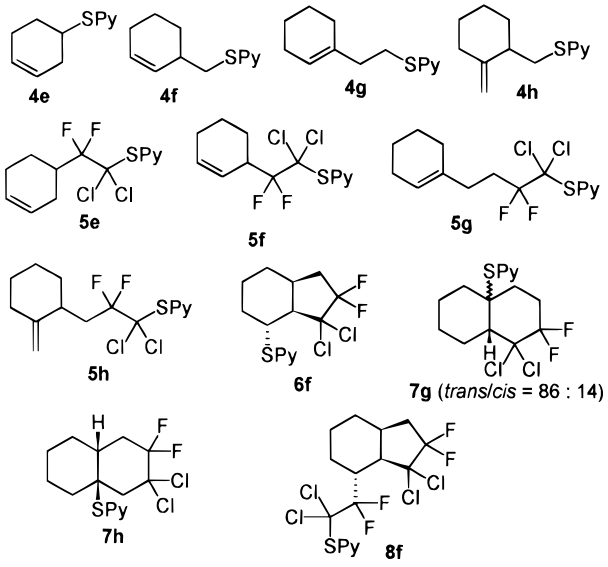
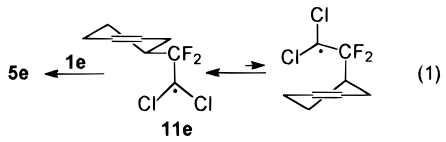


Chart 3



7d and **9d**. However, since 6-*endo* cyclization is kinetically unfavorable, the relative yield of the cyclic products **7d** and **9d** is lower than that in the reaction of **1b** in which the olefin also has two alkyl substituents.

Cyclohexanes and cyclohexenes have rather rigid conformations, and a higher selectivity of cyclization is expected. Such cyclization products may be important for the synthesis of fluorinated polycyclic compounds. Thus, several Barton esters with unsaturated cyclohexane moieties (**1e**−**h**) were prepared and the photoreaction with fluoroolefin **3** was examined. Photoreaction of 3-cyclohexenyl derivative **1e** gave no cyclized products. Cyclohexyl radicals react at the less-hindered site with sterically crowded radical acceptors such as **3** to give equatorially substituted adducts.[9,10] A similar stereochemistry for the cyclohexenyl radicals is anticipated, and the pseudo-equatorial dichlorodifluoroethyl radical **11e** is a conceivable intermediate. Interconversion between pseudo-equatorial and pseudo-axial conformers (eq 1) in



such a bulky substituent would be too slow for transannular cyclization, and rapid trapping of **11e** with the thiocarbonyl group of **1e** gives **5e**, while transannular cyclization of 4-cyclohexenylethyl radicals have been reported to yield a bicyclo[3.2.1]octane system.[11]

Barton ester **1f** selectively gave 5-*exo* cyclization products **6f** and **8f** as well as noncyclized **5f**. The proton noise-decoupled ^{13}C-NMR spectra indicated stereoselective formation with 14 signals (10 singlets, three doublets-of-doublets, and one doublet) for **6f** and 16 signals (seven singlets, five doublets of doublets, two triplets, and two doublets) for **8f**. However, the ^{1}H-NMR spectra (500 MHz) of the cyclized products did not represent their

(10) Okano, T.; Nakano, Y.: Takakura, N.; Eguchi, S. *The 50th Anniversary International Symposium on Organic Synthesis*; abstract PS-32; Soc. Synth. Org. Chem.: Tokyo, 1992.

(11) Chow, Y. L.; Perry, R. A. *Can. J. Chem.* **1985**, *63*, 2203. Weinges, K.; Reichert, H.; Huber-Patz, U.; Irngartinger, H. *Liebigs Ann. Chem.* **1993**, 403. Yadav, V.; Fallis, *Can. J. Chem.* **1991**, *69*, 779. Kraus, G. A.; Liras, S. *Tetrahedron Lett.* **1990**, *31*, 5265.

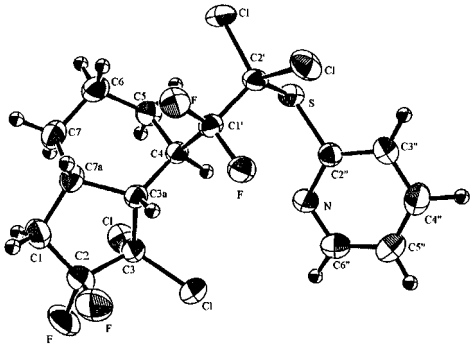
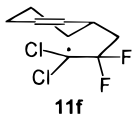


Figure 1. ORTEP plot of **8f**.

structures in a straigtforward manner. A quartet signal (J = 4 Hz) in the lower field region (δ 4.69) of **6f** reveals its hydroindane skeleton, since this signal can be assigned to the proton at the thiopyridyl-substituted carbon, which in the 6-*endo* products would presumably appear as a triplet due to coupling with only two vicinal hydrogens. The small coupling constant suggests that this thiopyridyl group occupies an axial position. Interconversion between pseudo-equatorial and pseudo-axial conformers is no longer necessary for the cyclization of the radical intermediate, since the distance from the radical center to the olefin in intermediate **11f** is shorter



11f

than that in **11e**. However, 1,3-transannular cyclization is unlikely to occur because of the expected increase in strain. The 1:2 adduct **8f** was crystallized, and X-ray crystallographic analysis revealed its stereochemistry as shown in Figure 1. Thus, the *cis*-hydrindane structure[12] of **6f** can be reasonably inferred from the structure of **8f** according to the same intermediacy of the 4-hydrindanyl radical to give both **6f** and **8f**. The dichlorodifluorothiopyridylethyl group in **8f** actually occupies an axial position of the cyclohexane ring, like the thiopyridyl group in **6f**, as assigned by the ^{1}H-NMR spectrum.

Selective 6-*endo* cyclization was also observed in the reaction of **1g**.[13] In this case, the ^{1}H NMR spectrum of the saturated product **7g** clearly shows a decalin structure by the absence of the lower-field signal which is expected in the 5-*exo* product. According to the ^{1}H- and ^{13}C-NMR spectra, **7g** is a 86:14 mixture of diastereomers. The major product was crystallized and the *trans*-decalin structure was established by X-ray crystallography (Figure 2). Similarly, selective 6-*endo* cyclization of **1h** to **7h** is supported by the ^{1}H-NMR spectrum, and the contrasting *cis*-decalin structure was also verified by X-ray crystallography (Figure 3). The ^{13}C-NMR spectrum of **7h** revealed its highly stereoselective formation, since no stereochemical counterpart was detected. This dramatic change in stereochemistry can be explained as schematically shown in Scheme 2. The initially formed

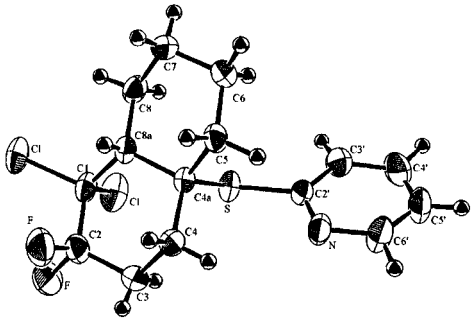


Figure 2. ORTEP plot of *trans*-**7g**.

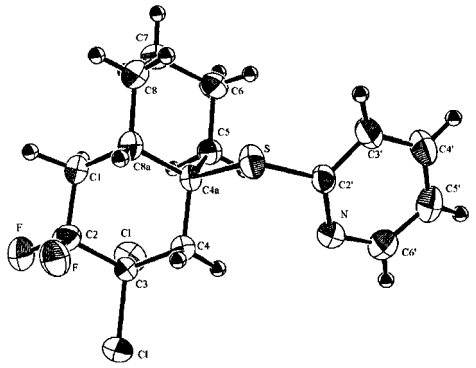
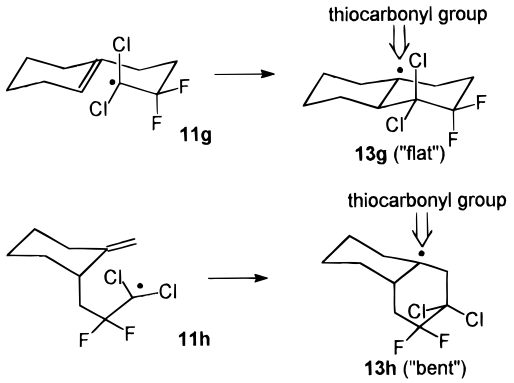


Figure 3. ORTEP plot of **7h**.

Scheme 2



radical intermediate **11g** in the reaction of **1g** cyclizes via a pseudo-equatorially substituted transition state to give a "flat" tertiary radical **13g**, and radical chain transfer then occurs by reaction with the thiocarbonyl group in **1g**, which approaches from the axial direction of the radical center. However, cyclization of **11h** occurs via an axially substituted conformation, since the maximum overlap between the radical center and the CC π-bond leads to a "bent" tertiary radical **13h**, in which the thiocarbonyl group of **1h** approaches from the axial direction of the radical center. These stereochemical consideration are consistent with 2-substituted cyclohexyl radicals,[9,10] even though the selective formation of *trans*-decalin from a related alkenyl radical has been reported.[14] It is noteworthy that the tertiary carbon radicals **13g** and **13h** did not give 1:2 adducts because of the higher steric hindrance around the radical center. The thiocarbonyl group, which is a less crowded radical acceptor, was the only trapping agent for these radicals.

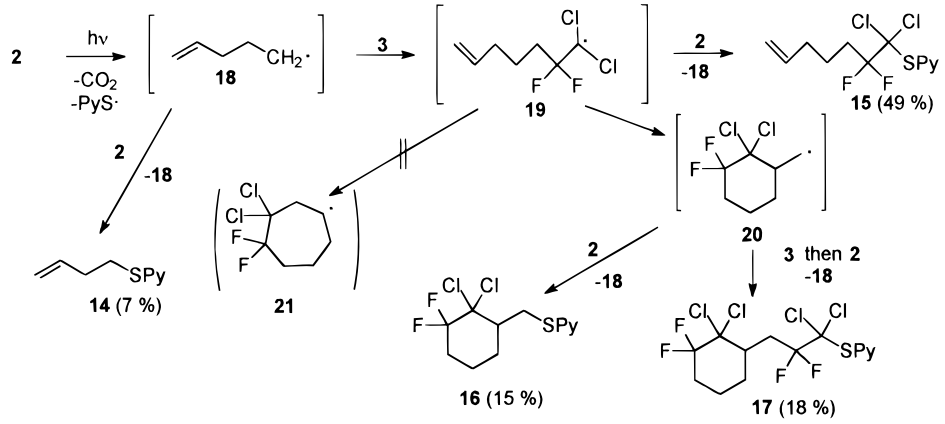
The radical reaction of **2** derived from 5-hexenoic acid was also examined, and again a relatively complex

(12) Stereoselective formation of *cis*-hydrindane from cyclohexenylpropyl radical has been reported: Curran, D. P.; Qi, H.; DeMello, N. C.; Lin, C.-H. *J. Am. Chem. Soc.* **1994**, *116*, 8430.

(13) In the reaction mixture, 3% yield of [4,4-dichloro-3,3-difluoro-4-(2-pyridylthio)butylidene]cyclohexane was found as an inseparable component of the mixture with **5g**. This 1:1 adduct was derived from the inseparable impurity contained in the starting cyclohexene-1-propionic acid. See the experimental section.

(14) Kawaguchi, M.; Satoh, S.; Mori, M.; Shibasaki, M. *Chem. Lett.* **1992**, 395.

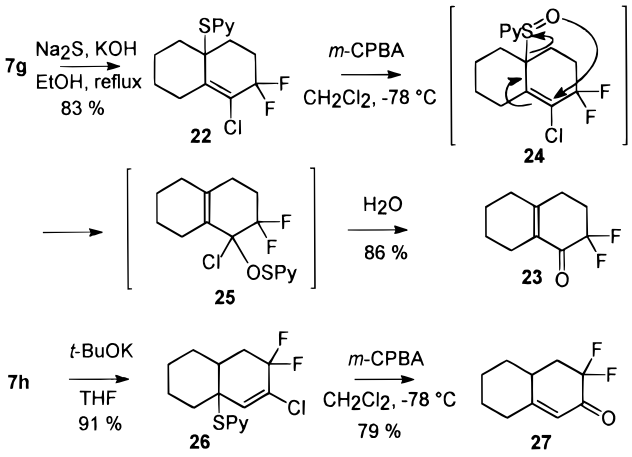
Scheme 3



mixture was obtained (Scheme 3). After chromatographic separation, self-trapping product **14** (7%), acyclic 1:1 adduct **15** (49%), 6-*exo* cyclization product **16** (14%), and 6-*exo* cyclization 1:2 adduct **17** (12%) were identified. The relative yield of the cyclized products [(**16** + **17**)/**15** = 0.53] is much smaller than that in the reaction of **1a** (0.82), indicating that cyclization of 6-heptenyl radicals is relatively less favorable.[15] Since the relative yields of the cyclization products were far lower than with the 3-butenyl radical, the substituent effect was not investigated further.

Alkyl-substituent effects in the radical cyclization of 5-hexenyl radicals have been extensively investigated, and the regiochemistry of the bonding terminal of a radical is known to be strongly affected by the alkyl substituents.[2] The regioselectivities of stable carbon radicals conjugated with electron-deficient groups change from kinetically controlled 5-*exo* cyclization to thermodynamically controlled 6-*endo* cyclization.[16] Although chlorine-substitution may stabilize the carbon radical, the majority of 5-*exo* products in the reaction of **1a** suggests the usual kinetic control of radical cyclization, as in the 5-*exo* cyclization of other dichloromethyl radicals.[17] Relative and absolute reaction rates of radical cyclization have been measured for the 5-hexenyl radicals with varous substituents on the vinyl group.[2c,18] It is interesting that the increase in 6-*endo* products in the radical cyclization of 5-substituted hexenyl radicals is not caused by the acceleration of 6-*endo* cyclization but rather by the reduction in the rate of 5-*exo* cyclization. Thus, under competitive reaction conditions, such as in the photodecomposition of Barton esters **1** in the presence of olefin **3**, the ratios of cyclized products to noncyclized addition products would be unchanged or smaller when the 6-*endo* products are predominant, since the reaction rates of linear radicals **11** with the thiocarbonyl group of the starting material would be comparable for the various substitution patterns of the olefinic moiety. However,

Scheme 4



the results described above show that the relative rates of cyclization are accelerated in the case of more-substituted olefins. Unlike the hexenyl radical, chlorinated radicals **11a**−**h** are highly electron-deficient, and substitution on the vinyl group with alkyl groups makes cyclization more favorable. While this acceleration may occur in both the 5-*exo* and 6-*endo* processes, the large steric effect of the bulky dichlorodifluoroalkyl radical and the substituted olefinic carbon center cancels the electronic effect and also determines the regiochemistry of the cyclization.

Conversion of Radical Adducts 7g and 7h to Difluorooctalones. Radical adducts like **5** were converted to the corresponding difluorocarboxylic acids by hydrolytic treatment with $AgNO_3$.[5] Similar treatment of the cyclized products **7g** and **7h** that were obtained in relatively good yields was expected to give products with a *gem*-difluorooctahydronaphthalenone structure. However, similar reaction conditions were completely ineffective against **7g** because two fluorine atoms prevented the generation of chlorinated carbocation at the α-position, where a π-participation effect by the thiopyridyl moiety is no longer available. Thus, we developed a new procedure for converting **7g** and **7h** to the fluorinated cycloalkenones (Scheme 4). Dehydrochlorination of **7g** was carried out with $Na_2S{\cdot}9H_2O$−KOH in refluxing EtOH to give **22** in 83% yield, and no dehydrofluorination was observed. Oxidation of the thioether group of **22** with *m*-CPBA at low temperature gave the desired 2,2-difluoro-1,2,3,4,5,6,7,8-octahydronaphthalen-1-one (**23**) in

(15) The 6-*exo* cyclization of heptenyl radical is 100 times slower than the 5-*exo* cyclization of hexenyl radical: Beckwith, A. L. J.; Schiesser, C. H., *Tetrahedron* **1985** *42*, 3925. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(16) Julia, M.; Le Goffic, F.; Katz, L. *Bull. Soc. Chim. Fr.* **1964**, 1122. Julia, M.; Le Goffic, F. *Bull. Soc. Chim. Fr.* **1964**, 1129.

(17) Nagashima, H.; Seki, K.; Ozaki, N.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *J. Org. Chem.* **1990**, *55*, 985. Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, *58*, 464. Nagashima, H.; Ozaki, N.; Seki, K.; Ishii, M.; Itoh, K. *J. Org. Chem.* **1989**, *54*, 4497. Takano, S.; Nishizawa, S.; Akiyama, M.; Ogasawara, K. *Synthesis* **1984**, 949.

(18) Van Tilborg, W. J. M.; Schaafsman, S. E.; Steinberg, H.; DeBoer, T. J. *Recl. Trav. Chim. Pay-Bas* **1967**, *86*, 417.

86% yield via [2,3]sigmatropic rearrangement[19] of allyl sulfoxide **24** to allyl sulfenate **25** followed by hydrolysis of the α-chlorosulfenate structure under acidic conditions. Isomeric **7h** was also dehydrochlorinated with more basic potassium *tert*-butoxide to give **26**, which was then converted into 3,3-difluoro-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (**27**) in good yield. These conversions of the radical reaction products into fluorinated cyclohexenones may be useful for the synthesis of fluorine-containing biologically active fused cyclohexenone compounds, such as steroids.

Experimental Section

^{1}H- and ^{13}C-NMR spectra of $CDCl_3$ solution were recorded in ppm (δ) at 200 and 50 MHz, respectively, with TMS as an internal standard if not noted otherwise. ^{19}F-NMR spectra of $CDCl_3$ solution were recorded at 87.67 MHz. Chemical shifts of the ^{19}F-NMR spectra were reported in ppm (δ) relative to internal $CFCl_3$.

Barton esters **1a**−**h** and **2** were prepared[4,5] by condensation of the corresponding carboxylic acids and *N*-hydroxy-2-pyridinethione with *N*,*N*-dicyclohexylcarbodiimide (DCC): a mixture of a carboxylic acid and equimolar amounts of *N*-hydroxy-2-pyridinethione and DCC in CH_2Cl_2 was stirred at room temperature for 2−4 h, and the formed dicyclohexylurea was filtered off in the dark. Removal of the solvent under reduced pressure gave a practically pure Barton ester in 70−98% yields. Freshly prepared Barton esters were used as quickly as possible without further purification.

General Procedure for the Photoreaction of Barton Esters 1a−h and 2 with 1,1-Dichloro-2,2-difluoroethene (3). An ice-cooled mixture of Barton ester and 10-fold amount of **3** in CH_2Cl_2 in a round-bottom flask equipped with a reflux condenser, in which −30 °C coolant (EtOH−H_2O) was circulated, was irradiated by a 500-W tungsten lamp until the yellow color of the solution was disappeared. After removal of the excess **3** by distillation at 30 °C, the solvent was removed under reduced pressure. The residue was chromatographed on a SiO_2 column eluting with *n*-hexane−EtOAc.

Photoreaction of 1a and 1 was performed as above using **1a** (837 mg, 4 mmol), **3** (4 mL, ca. 40 mmol), and CH_2Cl_2 (2 mL) with irradiation for 5 h.

1-(2-Pyridylthio)-3-butene (4a): 172 mg (26%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 2.40−2.50 (2H, m), 3.25 (2H, t, *J* = 7 Hz), 5.00−5.18 (2H, m), 5.90 (1H, ddt, *J* = 17, 10, 7 Hz), 6.95−7.00 (1H, m), 7.16−7.20 (1H, m), 8.44 (1H, br s).

1,1-Dichloro-2,2-difluoro-1-(2-pyridylthio)-5-hexene (5a): 417 mg (35%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 2.34−2.70 (4H, m), 5.02−5.20 (2H, tq-like m), 5.78−5.98 (1H, m), 7.37−7.43 (1H, m), 7.75−7.83 (1H, m), 7.86−7.90 (1H, m), 8.71 (1H, br s); ^{13}C-NMR ($CDCl_3$) 25.89 (t, *J* = 4 Hz), 31.67 (t, *J* = 25 Hz), 94.43 (t, *J* = 32 Hz), 116.24, 122.21 (t, *J* = 257 Hz), 124.98, 132.20, 136.63, 137.65, 151.01, 152.09; ^{19}F-NMR ($CDCl_3$) −104.1 (t, *J* = 17 Hz). MS *m*/*z* (%) 297 (M^+, 1.4), 110 (100). Anal. Calcd for $C_{11}H_{11}Cl_2F_2NS$: C, 44.31; H, 3.72, N; 4.77. Found: C, 44.37; H, 3.98; N, 4.38.

1,1-Dichloro-2,2-difluoro-5-[1-(2-pyridylthio)methyl]-cyclopentane (6a): 155 mg (13%); pale yellow oil; ^{1}H-NMR ($CDCl_3$, 500 MHz) 1.64−1.88 (1H, m), 2.05−2.57 (3H, m), 2.83−3.01 (1H, m), 3.26 (1H, dd, *J* = 14, 10 Hz), 3.82 (1H, dd, *J* = 14, 4 Hz), 7.01 (1H, ddd, *J* = 7, 4, 1 Hz), 7.19 (1H, dt, *J* = 7, 1 Hz), 7.50 (1H, td, *J* = 7, 1 Hz), 8.45 (1H, br d); ^{13}C-NMR ($CDCl_3$) 23.55 (d, *J* = 6 Hz), 29.07 (dd, *J* = 25, 21 Hz), 29.54, 49.60, 91.72 (dd, *J* = 28, 24 Hz), 120.10, 122.59, 125.94 (dd, *J* = 268, 253 Hz), 136.48, 150.03, 158.22; ^{19}F-NMR ($CDCl_3$) −94.4 (dt, *J* = 220, 23 Hz), −113.4 (d, *J* = 220 Hz); MS *m*/*z* (%) 297 (M^+, 31), 111 (100). Anal. Calcd for $C_{11}H_{11}Cl_2F_2NS$: C, 44.31; H, 3.72; N, 4.70. Found: C, 44.15; H, 3.70; N, 4.88.

1,1-Dichloro-2,2-difluoro-5-(2-pyridylthio)cyclohexane (7a): 48 mg (4%); pale yellow oil; ^{1}H-NMR ($CDCl_3$, 500 MHz) 1.82 (1H, qd, *J* = 14, 4 Hz), 2.21−2.30 (2H, m), 2.47 (1H, tdd, *J* = 14, 7, 2 Hz), 2.53−2.60 (1H, m), 3.04 (1H, dddd, *J* = 14, 5, 4, 3 Hz), 4.28 (1H, tt, *J* = 14, 4 Hz), 7.03 (1H, ddd, *J* = 8, 5, 1 Hz), 7.16 (1H, dt, *J* = 8, 1 Hz), 7.51 (1H, td, *J* = 8, 2 Hz), 8.46−8.47 (1H, m); ^{13}C-NMR ($CDCl_3$) 27.96 (d, *J* = 9 Hz), 30.63 (dd, *J* = 25, 22 Hz), 37.67, 49.00, 86.26 (dd, *J* = 30, 24 Hz), 119.08 (dd, *J* = 257, 247 Hz), 120.38, 123.09, 136.65, 150.23, 157.51; ^{19}F-NMR ($CDCl_3$) −106.2 (ddd, *J* = 231, 26, 11 Hz), −110.0 (d, *J* = 231 Hz); MS *m*/*z* (%) 297 (M^+, 41), 299 (15), 111 (100). Anal. Calcd for $C_{11}H_{11}Cl_2F_2NS$: C, 44.31; H, 3.72; N, 4.77. Found: C, 44.50; H, 3.74; N, 4.49.

1:1 Mixture of 1,1-Dichloro-2,2-difluoro-5-[3,3-dichloro-2,2-difluoro-3-(2-pyridylthio)propyl]cyclopentane (8a) and 5-[2,2-Dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]-1,1-dichloro-2,2-difluorocyclohexane (9a): 202 mg (12%: **8a**; 8%, **9a**; 4%: Yields were estimated from the relative intensities of the paired peaks in the ^{13}C-NMR spectrum); ^{1}H-NMR ($CDCl_3$) 1.71−3.50 (7H, m), 7.38−7.45 (1H, m), 7.76−7.90 (2H, m), 8.69−8.73 (1H, m); ^{13}C-NMR ($CDCl_3$) 22.61 (td, *J* = 8, 4Hz), 24.56 (dd, *J* = 7, 4 Hz), 29.35 (dd, *J* = 25, 21 Hz), 29.53 (t, *J* = 24 Hz), 32.68 (t, *J* = 22 Hz), 38.96 (t, *J* = 23 Hz), 43.67 (m), 45.10, 86.22 (dd, *J* = 32, 27 Hz), 92.00 (dd, *J* = 29, 24 Hz), 93.90 (t, *J* = 32 Hz), 93.98 (t, *J* = 34 Hz), 118.67 (dd, *J* = 257, 247 Hz), 120.26 (t, *J* = 248 Hz), 125.25, 122.26 (t, *J* = 258 Hz), 125.61 (t, *J* = 252 Hz), 132.41, 132.58, 137.79, 151.11, 151.74; ^{19}F-NMR ($CDCl_3$) −94.2 (0.7F, dt, *J* = 221, 26 Hz), −100.4 to −102.1 (2F, m), −104 to −102 (0.6F, m), −115.84 (0.7F, dd, *J* = 221, 7 Hz); MS *m*/*z* (%) 429 (M^+, 2), 78 (100). Anal. Calcd for $C_{13}H_{11}Cl_4F_4NS$: C, 36.22; H, 2.57; N 3.25. Found: C, 36.32; H, 2.70; N, 3.00.

Photoreaction of 1b and 3 was performed as above using **1b** (339 mg, 1.6 mmol), **3** (1.6 mL, ca. 16 mmol), and CH_2Cl_2 (2 mL) with irradiation for 5 h.

***(E)*-1-(2-Pyridylthio)-3-pentene (4b)**: 30 mg (11%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.665 (3H, d, *J* = 5 Hz), 2.395 (2H, m), 3.195 (2H, t, *J* = 7 Hz), 5.42−5.65 (2H, m), 6.967 (1H, ddd, *J* = 7, 5, 1 Hz), 7.175 (1H, dt, *J* = 8, 1 Hz), 7.471 (1H, ddd, *J* = 8, 7, 2 Hz), 8.428 (1H, ddd, *J* = 5, 2, 1 Hz).

***(E)*-1,1-Dichloro-2,2-difluoro-1-(2-pyridylthio)-5-heptene (5b)**: 27 mg (5%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.67 (3H, d, *J* = 4.8 Hz), 2.25−2.64 (4H, m), 5.38−5.65 (2H, m), 7.39 (1H, ddd, *J* = 7, 5, 1 Hz), 7.79 (1H, dt, *J* = 7, 2 Hz), 7.87 (1H, td, *J* = 7, 1 Hz), 8.71 (1H, dd, *J* = 5, 2 Hz); ^{13}C-NMR ($CDCl_3$) 17.94, 24.78 (t, *J* = 4 Hz), 32.35 (t, *J* = 23 Hz), 94.20 (t, *J* = 30 Hz), 122.24 (t, *J* = 257 Hz), 124.94, 126.94, 129.10, 132.14, 137.64, 151.00, 152.17; ^{19}F-NMR ($CDCl_3$) −104.2 (t, *J* = 17 Hz); MS *m*/*z* (%) 311 (M^+, 1), 111 (100). Anal. Calcd for $C_{12}H_{13}F_2Cl_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.17; H, 4.55; N, 4.14.

***erythro*-2,2-Dichloro-1,1-difluoro-3-[1-(2-pyridylthio)-ethyl]cyclopentane (6b*e*)**: 98 mg (34%); colorless solid; mp 60−61.5 °C; ^{1}H-NMR ($CDCl_3$) 1.73 (3H, d, *J* = 7 Hz), 1.73−1.95 (1H, m), 2.03−2.51 (3H, m), 2.73−2.90 (1H, m), 4.29 (1H, dqd, *J* = 11, 7, 1 Hz), 7.01 (1H, ddd, *J* = 7, 6, 1 Hz), 7.17 (1H, dt, *J* = 8, 1 Hz), 7.50 (1H, ddd, *J* = 8, 7, 2 Hz), 8.05 (1H, ddd, *J* = 6, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 21.54, 24.61 (t, *J* = 7 Hz), 28.16 (dd, *J* = 25, 20 Hz), 43.20, 53.57, 90.10 (dd, *J* = 28, 24 Hz), 120.26, 123.54, 126.15 (dd, *J* = 268, 251 Hz), 136.62, 150.05, 158.33; ^{19}F-NMR ($CDCl_3$) −95.1 (dt, *J* = 226, 25 Hz), −114.0 (d, *J* = 226 Hz); MS *m*/*z* (%) 311 (M^+, 9), 111(100). Anal. Calcd for $C_{12}H_{13}F_2Cl_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.30; H, 4.37; N, 4.19.

***threo*-2,2-Dichloro-1,1-difluoro-3-[1-(2-pyridylthio)ethyl]cyclopentane (6b*t*)**: 17 mg (6%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.54 (3H, d, *J* = 7 Hz), 1.78−2.00 (1H, m), 2.03−2.59 (3H, m), 2.89−3.04 (1H, m), 4.36 (1H, p, *J* = 7 Hz), 7.00 (1H, ddd, *J* = 7, 5, 1 Hz), 7.20 (1H, dt, *J* = 8, 1 Hz), 7.50 (1H, ddd, *J* = 8, 7, 2 Hz), 8.45 (1H, ddd, *J* = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 19.69, 22.34 (d, *J* = 7 Hz), 28.53 (dd, *J* = 25, 21 Hz), 39.67, 52.89, 91.00 (dd, *J* = 27, 24 Hz), 120.05, 123.57, 125.84 (dd, *J* = 267, 252 Hz), 136.47, 149.91, 158.54; ^{19}F-NMR ($CDCl_3$) −94.6 (dt, *J* = 215, 26 Hz), −114.4 (d, *J* = 215 Hz); MS *m*/*z* (%) 311 (M^+, 17), 111 (100). Anal. Calcd for $C_{12}H_{13}F_2Cl_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.18; H, 4.38; N, 4.42.

(19) Reich, H. J.; Yelm, K. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1983**, *105*, 2503. Garigipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861. Lambs, L.; Singh, N.; Biellmann, J.-F. *J. Org. Chem.* **1992**, *57*, 6301.

3,4-*trans*-2,2-Dichloro-1,1-difluoro-3-methyl-4-(2-pyridylthio)cyclohexane (7b): 23 mg (8%); colorless solid; mp 92−95 °C; ^{1}H-NMR ($CDCl_3$) 1.46 (3H, d, J = 6 Hz), 1.91 (1H, qd, J = 13, 4 Hz), 2.12−2.40 (2H, m), 2.42−2.71 (2H, m), 4.01 (1H, td, J = 13, 4 Hz), 7.01 (1H, ddd, J = 7, 5, 1 Hz), 7.18 (1H, dt, J = 8, 1 Hz), 7.50 (1H, ddd, J = 8, 7, 2 Hz), 8.44 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$)[20] 14.55, 28.99 (d, J = 8 Hz), 30.43 (dd, J = 24, 22 Hz), 44.34, 48.64, 119.37 (t, J = 252, 243 Hz), 120.33, 123.35, 136.74, 149.90, 157.89; ^{19}F-NMR ($CDCl_3$) −103.7 (d, J = 232 Hz), −107.2 (dd, J = 232, 19 Hz); MS m/z (%) 311 (M^+, 30), 111 (100). Anal. Calcd for $C_{12}H_{13}F_2Cl_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.37, H, 4.32, N, 4.18.

1:1 Mixture of 2,2-dichloro-1,1-difluoro-3-[4,4-dichloro-3,3-difluoro-4-(2-pyridylthio)but-2-yl]cyclopentane (8b) and 2,2-Dichloro-1,1-difluoro-3-methyl-4-[2,2-dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]cyclohexane (9b): 100 mg (14%: **8b**; 7%, **9b**; 7%; yields were estimated from the relative peak areas of the paired peaks in the ^{1}H-NMR spectrum); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.51 (1.5H, dd, J = 7, 2 Hz), 1.70 (1.5H, dd, J = 7, 3 Hz), 1.85−2.52 (4H, m), 2.76−2.94 (0.5H, m), 3.07−3.36 (1H, m), 3.37−3.66 (0.5H, m), 7.36−7.40 (1H, m), 7.74−7.90 (2H, m), 8.69−8.72 (1H, m); ^{13}C-NMR ($CDCl_3$) 12.39 (t, J = 5 Hz), 15.06 (dd, J = 9, 4 Hz), 19.31, (d, J = 6 Hz), 25.90 (dd, J = 12, 7 Hz), 28.10 (ddd, J = 25, 20, 3 Hz), 29.31, (dd, J = 25, 22 Hz), 36.75 (t, J = 23 Hz), 42.57 (dd, J = 23, 20 Hz), 47.82 (d, J = 7 Hz), 49.31 (d, J = 5 Hz), 90.6−95.6 (m), 116.4−131.0 (m), 125.12, 132.46, 137.69, 137.75, 151.05, 137.69, 137.75; ^{19}F-NMR ($CDCl_3$) −91.9 (d, J = 246 Hz), −92.7 (dt, J = 190, 22 Hz), −95.3 (dt, J = 190, 20 Hz), −103.9 (dd, J = 246 Hz), −104.7 (dd, J = 246, 20 Hz), −114.7 (dd, J = 170, 7 Hz), 117.3 (d, J = 170 Hz); MS (CI) m/z (%) 446 (M + H^+, 70), 446 (100). Anal. Calcd for $C_{14}H_{13}Cl_4F_4NS$: C, 37.78; H, 2.94, N, 3.15. Found: C, 37.89; H, 2.92, N, 3.04.

Photoreaction of 1c and 3 was performed as above using **1c** (763 mg, 3.0 mmol), **3** (3.0 mL, ca. 30 mmol), and CH_2Cl_2 (3 mL) with irradiation for 5 h.

4-Methyl-1-(2-pyridylthio)-3-pentene (4c): 120 mg (19%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.63 (3H, d, J = 1 Hz), 1.71 (3H, d, J = 1 Hz), 2.40 (2H, q, J = 7 Hz), 3.16 (2H, t, J = 7 Hz), 5.22 (1H, m, J = 7 Hz for a triplet), 6.98 (1H, ddd, J = 7, 5, 1 Hz), 7.16 (1H, dt, J = 8, 1 Hz), 7.47 (1H, ddd, J = 8, 7, 2 Hz), 8.44 (1H, ddd, J = 5, 2, 1 Hz).

2,2-Dichloro-1,1-difluoro-3-[2-(2-pyridylthio)prop-2-yl]-cyclopentane (6c): 546 mg (53%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.63 (3H, s), 1.89 (3H, s), 2.06−2.49 (4H, m), 3.82−3.95 (1H, m), 7.11 (1H, ddd, J = 7, 5, 1 Hz), 7.29 (1H, dt, J = 8, 1 Hz), 7.54 (1H, td, J = 8, 2 Hz), 8.50 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.95 (d, J = 2 Hz), 25.69, 28.03 (dd, J = 25, 21 Hz), 29.18, 53.60, 54.20, 90.86 (dd, J = 26, 23 Hz), 121.58, 125.78 (dd, J = 268, 253 Hz), 127.53, 136.72, 150.05, 158.13; ^{19}F-NMR ($CDCl_3$) −94.3 (dt, J = 218, 22 Hz), −114.2 (d, J = 218, 22 Hz); MS (CI) m/z (%) 337 (M + H^+, 100). Anal. Calcd for $C_{13}H_{15}F_2Cl_2NS$: C, 47.86; H, 4.63; N, 4.29. Found: C, 47.96; H, 4.79; N, 4.06.

2,2-Dichloro-1,1-difluoro-3-[3,3-difluoro-4,4-dichloro-2-methyl-3-(2-pyridylthio)but-2-yl]cyclopentane (8c): 94 mg (6%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.62 (3H, t, J = 2 Hz), 1.95 (3H, s), 2.07−2.52 (4H, m), 3.58−3.68 (1H, m), 7.41 (1H, ddd, J = 7, 5, 1 Hz), 7.80 (1H, dt, J = 7, 2 Hz), 7.88 (1H, td, J = 7, 1 Hz), 8.73 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 21.45 (t, J = 5 Hz), 21.65 (dd, J = 7, 3 Hz), 23.38 (t, J = 4 Hz), 28.03 (dd, J = 25, 21 Hz), 48.45 (t, J = 22 Hz), 50.17 (t, J = 4 Hz), 91.31 (t, J = 25 Hz), 94.86 (t, J = 37 Hz), 122.34 (t, J = 268 Hz), 125.13, 125.45 (t, J = 268 Hz), 132.80, 137.68, 150.99, 152.07; ^{19}F-NMR ($CDCl_3$) −92.5 (dt, J = 220, 25 Hz), −97.1 (s), −116.6 (d, J = 220 Hz); MS (CI) m/z (%) 458 (M + H^+, 72), 460 (100). Anal. Calcd for $C_{15}H_{15}F_4Cl_4NS$: C, 39.24; H, 3.29; N, 3.05. Found: C, 39.25; H, 3.43; N, 3.09.

Photoreaction of 1d and 3 was performed as above using **1d** (742 mg, 3.0 mmol), **3** (3.0 mL, ca. 30 mmol), and CH_2Cl_2 (3 mL) with irradiation for 5 h.

3-Methyl-1-(2-pyridylthio)-3-butene (4d): 124 mg (19%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.79 (3H, t, J = 1 Hz), 2.42 (2H, t, J = 7 Hz), 3.30 (2H, t, J = 7 Hz), 4.79−4.82 (2H, m), 6.98 (1H, ddd, J = 7, 5, 1 Hz), 7.18 (1H, dt, J = 8, 1 Hz), 7.48 (1H, ddd, J = 8, 7, 2 Hz), 8.44 (1H, ddd, J = 5, 2, 1 Hz).

1,1-Dichloro-2,2-difluoro-5-methyl-1-(2-pyridylthio)-5-hexene (5d): 249 mg (22%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.79 (3H, s), 2.29−2.37 (2H, m), 2.46−2.74 (2H, m), 4.75−4.81 (2H, m), 7.40 (1H, m), 7.75−7.90 (2H, m), 8.71 (1H, m); ^{13}C-NMR ($CDCl_3$) 22.57, 29.41 (t, J = 4 Hz), 30.66 (t, J = 23 Hz), 94.51 (t, J = 33 Hz), 111.21, 122.30 (t, J = 257 Hz), 124.97, 132.19, 137.65, 143.96, 151.00, 152.07; ^{19}F-NMR ($CDCl_3$) −104.4 (t, J = 17 Hz); MS m/z (%) 311 (M^+, 3), 78 (100). Anal. Calcd for $C_{12}H_{13}Cl_2F_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.24; H, 4.16; N, 4.52.

2,2-Dichloro-1,1-difluoro-4-methyl-4-(2-pyridylthio)cyclohexane (7d): 357 mg (38%); colorless solid; mp 69−70 °C; ^{1}H-NMR ($CDCl_3$) 1.70 (3H, s), 1.83−2.01 (1H, m), 2.18−2.59 (3H, m), 2.92 (1H, d, J = 15 Hz), 3.51 (1H, d, J = 15 Hz), 7.10 (1H, ddd, J = 7, 5, 1 Hz), 7.27 (1H, dt, J = 8, 1 Hz), 7.54 (1H, ddd, J = 8, 7, 2), 8.51 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 27.86 (t, J = 23 Hz), 28.31, 34.12 (t, J = 5 Hz), 49.68, 52.96, 85.58 (t J = 27 Hz), 119.15 (t, J = 252 Hz), 121.35, 126.85, 136.76, 150.02, 157.90; ^{19}F-NMR ($CDCl_3$) −107.22 (m); MS m/z (%) 311 (M^+, 25), 67 (100). Anal. Calcd for $C_{12}H_{13}Cl_2F_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.54; H, 4.39; N, 4.31.

2,2-Dichloro-1,1-difluoro-4-methyl-4-[2,2-dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]cyclohexane (9d): 133 mg (10%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.73 (3H, s), 1.96−2.64 (4H, m), 3.07 (1H, dd, J = 15, 2 Hz), 3.17 (1H, ddd, J = 15, 4, 2 Hz), 7.42 (1H, ddd, J = 8, 5, 1 Hz), 7.81 (1H, td, J = 8, 2 Hz), 7.88 (1H, dt, J = 8, 1 Hz), 8.74 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.85, 26.20 (t, J = 22 Hz), 28.53 (dd, J = 14, 7 Hz), 46.93 (t, J = 22 Hz), 48.55 (t, J = 5 Hz), 85.24 (dd, J = 30, 24 Hz), 94.37 (t, J = 36 Hz), 118.49 (dd, J = 256, 246 Hz), 121.47 (t, J = 267 Hz), 125.21, 132.80, 137.73, 151.01, 151.83; ^{19}F-NMR ($CDCl_3$) −102.3 (s), −106.5 (ddd, J = 238, 25, 7 Hz), −110.6 (d, J = 238 Hz); MS (CI) m/z (%) 444 (M + H^+, 76), 446 (100). Anal. Calcd for $C_{14}H_{13}Cl_4F_4NS$: C, 37.78; H, 2.94; N, 3.15. Found: C, 38.08; H, 2.95; N, 3.07.

Photoreaction of 1e and 3 was performed as above using **1e** (1000 mg, 4.25 mmol), **3** (4.0 mL, ca. 40 mmol), and CH_2Cl_2 (4 mL) with irradiation for 5 h.

4-(2-Pyridylthio)cyclohexene (4e): 107 mg (13%); ^{1}H-NMR ($CDCl_3$) 1.693−1.874 (1H, m), 2.06−2.28 (4H, m), 2.50−2.67 (1H, m), 4.04−4.17 (1H, m), 5.63−5.79 (2H, m), 6.97 (1H, ddd, J = 8, 5, 1 Hz), 7.18 (1H, dt, J = 8, 1 Hz), 7.47 (1H, ddd, J = 8, 8, 2 Hz), 8.43 (1H, ddd, J = 5, 2, 1 Hz).

4-[2,2-Dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]cyclohexene: 938 mg (68%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.62 (1H, ddd, J = 12, 9, 4 Hz), 2.11−2.38 (4H, m), 2.38−2.55 (1H, m), 2.74−3.03 (1H, m), 5.63−5.77 (2H, m), 7.39 (1H, ddd, J = 7, 5, 1 Hz), 7.79 (1H, td, J = 7, 2 Hz), 7.89 (1H, dt, J = 7, 1 Hz), 8.71 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 23.07 (dd, J = 8, 4 Hz), 25.06, 26.46 (dd, J = 8, 4 Hz), 38.98 (t, J = 23 Hz), 94.84 (t, J = 35 Hz), 121.88 (t, J = 259 Hz), 122.87, 125.38, 126.89, 132.22, 137.60, 150.89, 152.07; ^{19}F-NMR ($CDCl_3$) −101.5 (dd, J = 243, 12 Hz), −105.8 (dd, J = 243, 15 Hz); MS m/z (%) 323 (M^+, 4), 111 (100). Anal. Calcd for $C_{13}H_{13}Cl_2F_2NS$: C, 48.16; H, 4.04; N, 4.32. Found: C, 48.11; H, 4.22; N, 4.33.

Photoreaction of 1f and 3 was performed as above using **1f** (499 mg, 2.0 mmol), **3** (2.0 mL, ca. 20 mmol), and CH_2Cl_2 (2 mL) with irradiation for 5 h.

3-[(2-Pyridylthio)methyl]cyclohexene (4f): 77 mg (18%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.26−2.03 (6H, m), 2.36−2.53 (1H, m), 3.142 (1H, dd, J = 13, 7 Hz), 3.23 (1H, dd, J = 13, 6 Hz), 5.68−5.81 (2H, m), 6.96 (1H, ddd, J = 7, 5, 1 Hz), 7.18 (1H, dt, J = 8, 1 Hz), 7.46 (1H, ddd, J = 8, 7, 2 Hz), 8.42 (1H, ddd, J = 5, 2, 1 Hz).

3-[2,2-Dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]cyclohexene (5f): 109 mg (16%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.33−1.82 (3H, m), 1.88−2.06 (3H, m), 2.25−2.71 (3H, m), 5.64 (1H, br d, J = 10 Hz), 5.76 (1H, dtd, J = 10, 4, 2 Hz), 7.39 (1H, ddd, J = 7, 5, 2 Hz), 7.79 (1H, td, J = 7, 2 Hz), 7.87 (1H, dt, J = 7, 1 Hz), 8.71 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 21.06, 24.94, 29.63, 29.93, 38.07 (t, J = 22 Hz), 94.75

(20) The dichloromethylene carbon signal was not clearly identified due to the low signal-to-noise ratio.

(t, J = 32 Hz), 122.65 (t, J = 258 Hz), 124.93, 128.61, 130.81, 132.11, 137.64, 150.96, 152.12; ^{19}F-NMR ($CDCl_3$) −102.0 (dd, J = 37, 15 Hz); MS m/z (%) 337 (M^+, 6), 112 (100). Anal. Calcd for $C_{14}H_{15}F_2Cl_2NS$: C, 49.71; H, 4.47; N, 4.14. Found: C, 49.89; H, 4.42; N, 3.95.

(3aR*,4S*,7aR*)-3,3-Dichloro-2,2-difluoro-4-(2-pyridylthio)perhydroindene (6f): 195 mg (29%); colorless solid; mp 96−99 °C; ^{1}H-NMR (500 MHz; $CDCl_3$) 1.60−1.65 (2H, m), 1.70−1.75 (1H, m), 1.80−1.85 (1H, m), 1.89 (1H, ddd, J = 15, 10, 5 Hz), 2.10 (1H, dddd, J = 32, 15, 9, 6 Hz), 2.33 (1H, ddd, J = 19, 10, 5 Hz), 2.47−2.54 (1H, m), 2.56 (1H, ddd, J = 19, 14, 10 Hz), 2.91 (1H, dt, J = 8, 4 Hz), 4.69 (1H, q, J = 4 Hz), 7.02 (1H, ddd, J = 7, 5, 1 Hz), 7.21 (1H, dt, J = 8, 1 Hz), 7.51 (1H, ddd, J = 8, 5, 2 Hz), 8.48 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.29, 28.42, 29.39, 29.78 (d, J = 6 Hz), 37.05 (dd, J = 24, 20 Hz), 39.20, 52.31, 90.69 (dd, J = 27, 24 Hz), 120.35, 123.59, 125.06 (dd, J = 268, 252 Hz), 136.73, 149.87, 157.98; ^{19}F-NMR ($CDCl_3$) −115.2 (dd, J = 221, 8 Hz), −95.2 (ddd, J = 221, 32, 16 Hz); MS (CI) m/z (%) 338 (M + H^+, 100). Anal. Calcd for $C_{14}H_{15}Cl_2F_2NS$: C, 49.71; H, 4.47; N, 4.14. Found: C, 49.67; H, 4.33; N, 4.30.

(3aR*,4R*,7aS*)-3,3-Dichloro-2,2-difluoro-4-[2,2-dichloro-1,1-difluoro-2-(2-pyridylthio)ethyl]perhydroindene (8f): 212 mg (22%); pale yellow solid; mp 70−78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) 1.50−1.62 (2H, m), 1.63−1.67 (1H, m), 1.89−1.93 (1H, m), 2.05−2.17 (2H, m), 2.42−2.48 (2H, m), 2.63 (1H, ddd, J = 22, 15, 10 Hz), 3.23 (1H, dd, J = 9, 3 Hz), 3.53 (1H, ddd, J = 22, 16, 6 Hz), 7.40 (1H, ddd, J = 7, 5, 2 Hz), 7.79 (1H, td, J = 7, 2 Hz), 7.88 (1H, ddd, J = 7, 2, 1 Hz) 8.72 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.41, 22.99 (dd, J = 5, 4 Hz), 30.30 (d, J = 7 Hz), 30.61, 37.08 (t, J = 21 Hz), 37.67 (dd, J = 25, 20 Hz), 45.88 (d, J = 6 Hz), 91.40 (dd, J = 26, 25 Hz), 94.22 (t, J = 35 Hz), 122.43 (dd, J = 266, 261 Hz), 124.94 (dd, J = 268, 253 Hz), 125.11, 132.52, 137.68, 151.08, 151.96; ^{19}F-NMR ($CDCl_3$) −116.0 (dd, J = 221, 10 Hz), −100.1 (dd, J = 247, 21 Hz), −93.7 (ddd, J = 221, 32, 20 Hz), −91.5 (dd, J = 247, 15 Hz); MS (CI) m/z (%) 472 (M + H^+, 100). Anal. Calcd for $C_{16}H_{15}Cl_4F_4NS$: C, 40.79; H, 3.21; N, 2.97. Found: C, 40.83; H, 3.30; N, 2.83.

Photoreaction of 1g and 3 was performed as above using **1g** (790 mg, 3.0 mmol), which contains 5% of cyclohexylidene isomer **10**, **3** (3.0 mL, ca. 30 mmol), and CH_2Cl_2 (3 mL) with irradiation for 5 h.

1-[2-(2-Pyridylthio)ethyl]cyclohexene (4g): 152 mg (23%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.50−1.68 (4H, m), 1.96−2.02 (4H, m), 2.33 (2H, t, J = 7.6 Hz), 3.21−3.29 (2H, m), 5.51 (1H, m), 6.96 (1H, ddd, J = 7, 5, 1 Hz), 7.17 (1H, dt, J = 8, 1 Hz), 7.46 (1H, dt, J = 8, 7, 2 Hz), 8.426 (1H, ddd, J = 5, 2, 1 Hz).

2:1 Mixture of 1-[4,4-dichloro-3,3-difluoro-4-(2-pyridylthio)butyl]cyclohexene (5g) and [4,4-dichloro-3,3-difluoro4-(2-pyridylthio)butylidene]cyclohexane:[13] 84 mg (8%: **5g**; 5%); pale yellow oil; ^{1}H-NMR ($CDCl_3$) 1.53−1.70 (5.33H, m), 1.91−2.04 (2.67H, m), 2.16−2.29 (2.67H, m), 2.42−2.68 (1.33H, m), 3.20 (0.67H, td, J = 18, 7 Hz), 5.20 (0.33H, tt, J = 7, 1 Hz), 5.50 (0.67H, m), 7.35−7.43 (1H, m), 7.74−7.83 (1H, m), 7.88 (1H, dt, J = 7, 1 Hz), 8.69−8.73 (1H, m); ^{19}F-NMR ($CDCl_3$) −104.5 (t, J = 19 Hz, 0.67F), −102.9 (t, J = 18 Hz; 0.33F); GC-MS m/z (%) **5g**; 351 (M^+, 5),111 (100). Anal. Calcd for $C_{15}H_{17}Cl_2F_2NS$: C, 51.14; H, 4.86; N, 3.98. Found: C, 51.21; H, 4.68; N, 4.28.

1,1-Dichloro-2,2-difluoro-4a-(2-pyridylthio)decahydronaphthalene (7g): 569 mg (54%); colorless solid; mp 76−98 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) 1.161 (1H, ddd, J = 14, 13, 4 Hz), 1.36−1.45 (2H, m), 1.64 (2H, t, J = 18 Hz), 1.91−2.03 (2H, m), 2.11−2.21 (2H, m), 2.26 (2H, br d, J = 25 Hz), 3.01 (1H, dd, J = 7, 4 Hz), 3.04−3.06 (1H, m), 7.10 (1H, ddd, J = 8, 5, 1 Hz), 7.40 (1H, d, J = 8 Hz), 7.53 (1H, td, J = 8, 2 Hz), 8.48 (1H, dd, J = 5, 1 Hz); recognizable minor peaks of the stereoisomer, 3.07 (ddd, J = 8, 4, 1 Hz), 3.13 (dd, J = 16, 4 Hz), 7.32 (d, J = 8 Hz), 8.51 (dd, J = 5, 1 Hz); ^{13}C-NMR ($CDCl_3$) 21.28, 22.73, 25.94, 27.83 (dd, J = 24, 22 Hz), 34.39 (d, J = 9 Hz), 57.87, 58.54, 90.85 (d, J = 29, 23 Hz), 119.72 (d, J = 258, 246 Hz), 121.95, 129.00, 136.99, 150.01, 156.93; recognizable minor peaks of the stereoisomer, 21.05, 38.07, 56.31, 122.28, 128.47, 150.20; ^{19}F-NMR ($CDCl_3$) −100.6 (ddd, J = 238, 32, 7 Hz), −105.7 (d, J = 238 Hz); MS m/z (%) 351 (M^+, 5), 111 (100). Anal. Calcd for $C_{15}H_{17}Cl_2F_2NS$: C, 51.14; H, 4.86; N, 3.98. Found: C, 51.04; H, 4.76; N, 4.19.

Photoreaction of 1h and 3 was performed as above using **1h** (915 mg, 3.5 mmol) **3** (4.0 mL, ca. 40 mmol), and CH_2Cl_2 (4 mL) with irradiation for 5 h.

1-Methylene-2-[(2-pyridylthio)methyl]cyclohexane (4h): 107 mg (14%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.25−1.76 (5H, m), 1.89−2.12 (2H, m), 2.24−2.48 (2H, m), 3.26 (1H, dd, J = 13, 8 Hz), 3.48 (1H, dd, J = 13, 7 Hz), 4.71 (1H, s), 4.77 (1H, s), 6.96 (1H, ddd, J = 7, 5, 1 Hz), 7.17 (1H, dt, J = 8, 1 Hz), 7.46 (1H, ddd, J = 8, 7, 2 Hz), 8.43 (1H, ddd, J = 5, 2, 1 Hz).

1-Methylene-2-[2,2-difluoro-3,3-dichloro-3-(2-pyridylthio)propyl]cyclohexane (5h): 87 mg (7%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.33−1.80 (5H, m), 1.87−1.99 (1H, m), 2.04−2.17 (1H, m), 2.24−2.35 (1H, m), 2.35−2.56 (1H, m), 2.61−2.68 (1H, m), 2.70−2.96 (1H, m), 4.67 (1H, s), 4.72 (1H, s), 7.39 (1H, ddd, J = 8, 4, 1 Hz), 7.79 (1H, td, J = 7, 2Hz), 7.88 (1H, d, J = 8 Hz), 8.71 (1H, d, J = 4 Hz); ^{13}C-NMR ($CDCl_2$) 24.20, 28.60, 34.35 (t, J = 23 Hz), 34.45 (d, J = 2 Hz), 34.98, 37.39 (d, J = 2 Hz), 94.95 (t, J = 33Hz), 106.66, 122.72 (t, J = 258 Hz), 124.95, 132.16, 137.65, 150.99, 151.78, 152.16; ^{19}F-NMR ($CDCl_3$) −100.6 (ddd, J = 236, 30, 12 Hz), −104.1 (ddd, J = 236, 25, 10 Hz); MS (CI) m/z (%) 352 (M + H^+, 100). Anal. Calcd for $C_{15}H_{17}Cl_2F_2NS$; C, 51.14; H, 4.86; N, 3.98. Found: C, 50.92; H, 4.85; N, 3.93.

***cis*-3,3-Dichloro-2,2-difluoro-4a-(2-pyridylthio)decahydronaphthalene (7h)**: 631 mg (52%); colorless solid; mp 94−96 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) 1.33 (1H, tt, J = 13, 3 Hz), 1.36−1.40 (1H, m), 1.54−1.62 (2H, m), 1.86−1.89 (1H, m), 1.92 (1H, tt, J = 13, 3 Hz), 2.00 (1H, ddd, J = 18, 7, 4 Hz), 2.23 (1H, tq, J = 13, 2 Hz), 2.58−2.65 (2H, m), 2.70 (1H, dt, J = 33, 14 Hz), 3.32 (1H, dd, J = 15, 5 Hz), 3.58 (1H, dd, J = 15, 2 Hz), 7.10 (1H, ddd, J = 7, 4, 1 Hz), 7.30 (1H, d, J = 7 Hz), 7.54 (1H, td, J = 7, 2 Hz), 8.52 (1H, dd, J = 4, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.24, 22.129, 26.45, 29.57, 32.62 (dd, J = 23, 21 Hz), 32.64 (d, J = 2 Hz), 54.52, 55.82, 85.81 (dd, J = 29, 24 Hz), 119.49 (dd, J = 256, 247 Hz), 121.58, 127.48, 136.82, 150.22, 157.35; ^{19}F-NMR ($CDCl_3$) −102.6 (ddd, J = 236, 32, 8 Hz), −107.4 (d, J = 236 Hz); MS (CI) m/z (%) 352 (M + H^+, 100). Anal. Calcd for $C_{15}H_{17}Cl_2F_2NS$; C, 51.14; H, 4.86; N, 3.98. Found: C, 51.13; H, 4.96; N, 4.01.

Photoreaction of 2 and 3 was performed as above using **2** (592 mg, 2.65 mmol), **3** (2.5 mL, ca. 25 mmol), and CH_2Cl_2 (2.5 mL) with irradiation for 3 h.

4-(2-Pyridylthio)-1-pentene (14): 34 mg (7%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.82 (2H, quintet, J = 7 Hz); 2.15−2.28 (2H, m), 3.19 (2H, t, J = 7 Hz), 4.96−5.12 (2H, m), 5.83 (1H, ddt, J = 17, 10, 7Hz), 6.97 (1H, ddd, J = 7, 5, 1 Hz), 7.18 (1H, dt, J = 8, 1 Hz), 7.48 (1H, ddd, J = 8, 7, 2 Hz), 8.43 (1H, ddd, J = 5, 2, 1 Hz).

6,6-Dichloro-5,5-difluoro-6-(2-pyridylthio)-1-heptene (15): colorless oil; 408 mg (49%); ^{1}H-NMR ($CDCl_3$) 1.71−1.83 (2H, m), 2.32−2.60 (2H, m), 4.99−5.13 (2H, m), 5.12 (2H, br q, J = 7 Hz), 5.82 (1H, ddt, J = 17, 10, 7 Hz), 7.39 (1H, ddd, J = 8, 5, 1 Hz), 7.79 (1H, td, J = 8, 2 Hz), 7.88 (1H, ddd, J = 8, 1, 1 Hz), 8.705 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.85 (t, J = 3 Hz), 31.52 (t, J = 24 Hz), 33.10, 94.58 (t, J = 33 Hz), 115.95, 122.45 (t, J = 256 Hz), 124.94, 137.64, 137.87, 150.97, 152.11; ^{19}F-NMR ($CDCl_3$) −103.9 (t, J = 19 Hz); MS (CI) 312 (M + H^+, 100). Anal. Calcd for $C_{12}H_{13}Cl_2F_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.27; H, 4.20; N, 4.38.

2,2-Dichloro-1,1-difluoro-3-[(2-pyridylthio)methyl]cyclohexane (16): 122mg (15%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.36−1.85 (3H, m), 2.07−2.58 (4H, m) 3.141 (1H, dd, J = 14, 10, 1 Hz), 4.02 (1H, dd, J = 14, 3, 1 Hz), 7.00 (1H, ddd, J = 7, 5, 1 Hz), 7.21 (1H, dt, J = 8, 1 Hz), 7.50 (1H, ddd, J = 8, 7, 2 Hz), 8.45 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.13 (dd, J = 7, 3 Hz), 26.90, 30.58 (t, J = 22 Hz), 30.71, 49.80, 92.69 (dd, J = 28, 24 Hz), 120.04 (dd, J = 264, 245 Hz), 120.03, 122.32, 136.47, 149.99, 158.49; ^{19}F-NMR ($CDCl_3$) −105.0 (m); MS m/z (%) 311 (M^+, 100). Anal. Calcd for $C_{12}H_{13}Cl_2F_2NS$: C, 46.17; H, 4.20; N, 4.49. Found: C, 46.45; H, 4.43; N, 4.44.

2,2-Dichloro-1,1-difluoro-3-[3,3-dichloro-2,2-difluoro-3-(2-pyridylthio)propyl]cyclohexane (17): 168 mg (18%);

colorless oil; ^{1}H-NMR ($CDCl_3$) 1.49−1.88 (3H, m), 2.03−2.74 (5H, m), 3.11−3.39 (1H, m), 7.410 (1H, ddd, J = 8, 5, 2 Hz), 7.80 (1H, td, J = 8, 2 Hz), 7.88 (1H, ddd, J = 8, 2, 1 Hz), 8.71 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 20.16 (d, J = 9 Hz), 28.98 (d, J = 4Hz), 30.39 (dd, J = 24, 21 Hz), 34.02 (td, J = 21, 2 Hz), 44.71, 92.63 (dd, J = 29, 23 Hz), 94.13 (t, J = 32 Hz), 119.72 (dd, J = 257, 248 Hz), 122.23 (t, J = 258 Hz), 125.17, 132.34, 137.76, 151.05; ^{19}F-NMR ($CDCl_3$) −100.8 to −102.6 (m), −103.8 to −105.5 (m); MS *m*/*z* (%) 443 (M^+, 6), 78 (100). Anal. Calcd for $C_{14}H_{13}Cl_4F_4NS$: C, 37.78; H 2.94; N, 3.15. Found: C, 37.80; H, 2.95; N, 3.13.

1-Chloro-2,2-difluoro-4a-(2-pyridylthio)-2,3,4,4a,5,6,7,8-octahydronaphthalene (22). A mixture of **7g** (829 mg, 2.35 mmol), $Na_2S{\cdot}9H_2O$ (565 mg, 2.53 mmol), and KOH (85%, 132 mg, 2.00 mmol) dissolved in 95% aqueous EtOH (6 mL) was refluxed for 5 h. Then, the solvents were removed under the reduced pressure. The resulting mixture was chromatographed on a SiO_2 column eluting with hexane−CH_2Cl_2 (1:1.5) to give **14** as pale yellow oil: 620 mg (83%); ^{1}H-NMR ($CDCl_3$) 1.24−1.61 (3H, m), 1.80 (1H, tdd, J = 14, 3, 2 Hz), 1.89−2.01 (1H, m), 2.07 (1H, tt, J = 13, 4 Hz), 2.17−2.43 (3H, m), 2.72 (1H, dddd, J = 32, 14, 10, 3 Hz), 2.70−2.92 (1H, m), 2.99 (1H, ddt, J = 15, 4, 2 Hz), 7.14 (1H, ddd, J = 8, 5, 1 Hz), 7.37 (1H, dt, J = 8, 1 Hz), 7.57 (1H, ddd, J = 8, 8, 2 Hz), 8.51 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 21.35, 25.90, 27.31, 29.88 (t, J = 24 Hz), 32.41 (d, J = 8 Hz), 38.03, 57.48, 117.08 (t, J = 237 Hz), 122.17, 124.95 (t, J = 28 Hz), 128.54, 144.60 (dd, J = 7, 5 Hz), 150.39, 156.87; ^{19}F-NMR ($CDCl_3$) −90.0 (ddd, J = 252, 32, 17 Hz), −95.4 (d, J = 252 Hz); MS *m*/*z* (%) 315 (M^+, 27), 111 (100). Anal. Calcd for $C_{15}H_{16}ClF_2NS$: C, 57.05; H, 5.11; N, 4.44. Found: C, 57.22; H, 4.94; N, 4.45.

2,2-Difluoro-1,2,3,4,5,6,7,8-octahydronaphthalen-1-one (23). To a stirred solution of **22** (316 mg, 1.00 mmol) in CH_2Cl_2 (20 mL) was added a solution of *m*-CPBA (70%, 320 mg, 1.30 mmol) in CH_2Cl_2 (20 mL) in 5 min at −78 °C under N_2 atmosphere. The mixture was stirred at −78 °C for 8 h, and then $(CH_3)_2S$ (0.5 mL) was added. The mixture was allowed to warm up to room temperature, washed with saturated aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on a SiO_2 column eluting with hexane−EtOAc (5:1) to give **17** as colorless oil: 160 mg (86%); ^{1}H-NMR ($CDCl_3$) 1.62−1.69 (4H, m), 2.20−2.30 (4H, m), 2.31−2.44 (2H, m), 2.45−2.54 (2H, m); ^{13}C-NMR ($CDCl_3$) 21.39, 21.65, 21.98, 28.21 (t, J = 5 Hz), 31.48 (t, J = 23 Hz), 31.90, 113.46 (t, J = 247 Hz), 131.43, 159.47, 185.95 (t, J = 25 Hz); ^{19}F-NMR ($CDCl_3$) −107.7 (ddd, J = 268, 32, 12 Hz), −114.1 (ddd, J = 268, 12, 7 Hz); IR (neat film) 1694, 1630 cm^{-1}; MS *m*/*z* (%) 186 (M^+, 94), 122 (100). Anal. Calcd for $C_{10}H_{12}F_2O$: C, 64.51; H, 6.50. Found: C, 64.72; H, 6.27.

3-Chloro-2,2-difluoro-4a-(2-pyridylthio)-1,2,4a,5,6,7,8,8a-octahydronaphthalene (26). A mixture of **7h** (1.41 g, 4.00 mmol) and *t*-BuOK (628 mg, 5.60 mmol) dissolved in anhydrous THF (50 mL) was stirred under refluxing for 2 h. The solvent was removed under reduced pressure. The residue was extracted with Et_2O (20 mL × 3), and the combined extracts were washed with saturated aqueous NaCl (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed by eluting with hexane−CH_2Cl_2 (2:1) to give pure **26** as pale yellow oil: 1.15 g (90%); ^{1}H-NMR ($CDCl_3$) 1.38−1.59 (4H, m), 1.63−1.79 (2H, m), 1.85−1.94 (1H, m), 1.97−2.13 (2H, m), 2.34 (1H, ddd, J = 28.8, 14, 10 Hz), 2.42−2.63 (2H, m), 6.57 (1H, t, J = 2 Hz), 7.13 (1H, ddd, J = 8, 5, 1 Hz), 7.32 (1H, dt, J = 8, 1 Hz), 7.56 (1H, ddd, J = 8, 8, 2 Hz), 8.51 (1H, ddd, J = 5, 2, 1 Hz); ^{13}C-NMR ($CDCl_3$) 22.11, 22.28, 27.17, 33.82, 35.94, 36.40 (t, J = 23 Hz), 55.88, 116.72 (t, J = 238 Hz), 121.95, 126.55 (t, J = 30 Hz), 127.81, 136.86, 140.89 (t, J = 6 Hz), 150.27, 156.74; ^{19}F-NMR ($CDCl_3$) −92.8 to −93.8 (m); MS *m*/*z* (%) 315 (M^+, 17), 111 (100). Anal. Calcd for $C_{15}H_{16}ClF_2NS$: C, 57.05; H, 5.11; N, 4.44. Found: C, 57.37; H, 5.19; N, 4.20.

3,3-Difluoro-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (27) was obtained in a manner similar to that for **23** from **26** (317 mg, 1.00 mmol), *m*-CPBA (70%, 320 mg, 1.3 mmol), and CH_2Cl_2 (40 mL): 132 mg (79%); colorless oil; ^{1}H-NMR ($CDCl_3$) 1.20−1.65 (3H, m), 1.84−2.17 (3H, m), 2.27 (1H, td, J = 13, 5 Hz), 2.47−2.73 (3H, m), 5.95 (1H, dd, J = 4, 2 Hz); ^{13}C-NMR ($CDCl_3$) 25.07, 26.81, 34.60, 35.64, 36.74 (dd, J = 7, 2 Hz), 37.88 (dd, J = 23, 21 Hz), 113.41 (dd, J = 250, 244 Hz), 121.93, 170.51, 186.39 (t, J = 25 Hz); ^{19}F-NMR ($CDCl_3$) −107.6 (ddd, J = 268, 32, 12 Hz), −114.0 (ddd, J = 268, 12, 7 Hz); MS *m*/*z* (%) 186 (M^+, 91), 122 (100). Anal. Calcd for $C_{10}H_{12}F_2O$: C; 64.51; H, 6.50. Found: C, 64.41; H, 6.60.

X-ray Structure Determination of 8f, 7g, and 7h. Colorless crystals of **8f**, **7g**, and **7h** were obtained by layering concentrated solutions in benzene. The crystal of **7g** was identical with the major product of **7g**, which was confirmed by the ^{1}H NMR spectrum. All measurements were made on a Rigaku diffractometer (AFC5R) with Mo Kα radiation. Each cell constant and orientation matrix for data collection were obtained from least squares refinement using the setting of 25 reflections in the each given range as below, and the individual crystallographic data are as follows. The data were collected at 23 °C using the $\omega-2\theta$ scan technique (2θ < 55.0°). Scans of (A + 0.30 tan θ)° (A = 1.31 for **8f** and **7h**, A = 1.89 for *trans*-**7g**) were made at a speed of 32.0°/min. The intensities of three representative reflections which were measured after every 150 reflections, and no crystal decay was noticed. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final least-squares refinement was based on the number of observed reflections with [$I > 3.0\sigma(I)$]. All calculations were performed using the TEXSAN crystallographic software package (1985).

Summary of Crystal Data. 8f:[21] setting angle, 29.63 < 2θ < 29.94°; monoclinic cell; dimensions, a = 9.053(2) Å, b = 11.292(1) Å, c = 18.624(1) Å, β = 90.337(8)°; Z = 4; V = 1903.8(1) Å^3; space group, $P2_1/n$; D_{calcd} = 1.644 g/cm^3; empirical formula $C_{16}H_{15}Cl_4F_4NS$; number of unique reflections = 4596 (R_{int} = 0.016); number of observations = 3323; R = 0.031; R_w = 0.041.

7g:[21] setting angle, 8.56 < 2θ < 17.20°; triclinic cell; dimensions, a = 10.234(7) Å, b = 10.992(9) Å, c = 7.435(3) Å, α = 102.91(6)°, β = 94.81(6)°, γ = 72.96(6)°; Z = 2; V = 779 (1) Å^3; space group, $P1$; D_{calcd} = 1.501 g/cm^3; empirical formula $C_{15}H_{17}Cl_2F_2NS$; number of unique reflections = 3573 (R_{int} = 0 .014); number of observations = 2599; R = 0.045; R_w = 0.058.

7h:[21] setting angle, 27.26 < 2θ < 29.58°; monoclinic cell; dimensions, a = 7.786(2) Å, b = 12.882(2) Å, c = 15.897(2) Å, β = 102.63(2)°; Z = 4; V = 1555.9 (5) Å^3; space group, $P2_1/c$; D_{calcd} = 1.504 g/cm^3; empirical formula $C_{15}H_{17}Cl_2F_2NS$; number of unique reflections = 3738 (R_{int} = 0 .027); number of observations = 2924; R = 0.048; R_w = 0.064.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Development of Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan (07555285).

JO970639U

(21) The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.