

Tetrathiafulvalenylallene: A New Class of Donor Molecules Having Strong Chiroptical Properties in Neutral and Doped States

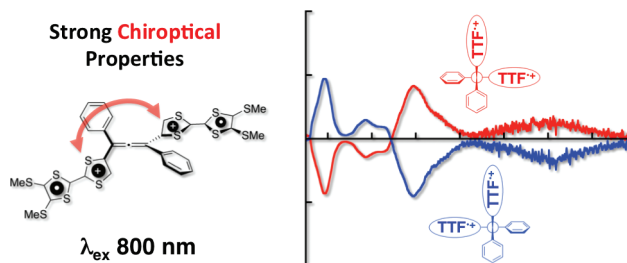
Masashi Hasegawa,* Yasuto Sone, Seiya Iwata, Hideyo Matsuzawa,
and Yasuhiro Mazaki*

Department of Chemistry, School of Science, Kitasato University, Sagamihara,
Kanagawa 252-0373, Japan

masasi.h@kitasato-u.ac.jp; mazaki@kitasato-u.ac.jp

Received July 14, 2011

ABSTRACT



A chiral tetrathiafulvalene (TTF) dimer bridged by an allene framework (**1**) was synthesized. An X-ray analysis of **1** revealed an effective conjugation between TTF and the allene backbone. Allene **1** was resolved into both enantiomers, which showed strong chiroptical electrochromic properties. Absolute configuration of the allene was validated by theoretical study of the electronic circular dichroism (ECD) spectrum. ECD spectra of cationic species 1^{2+} and 1^{4+} exhibited intense Cotton Effects over the visible region.

The design and synthesis of redox-mediated chiroptical organic materials have attracted considerable attention because of their potential applications for photonic devices related to polarized light, including optical switches, memory, and optical modulators that have chiroptical properties.¹ A wealth of redox systems with asymmetric units based on diverse platforms have been prepared thus far.^{1–4} In most of these chiral systems, polymeric or oligomeric donor molecules having chiral alkyl groups are employed. The chiral side chain often gives rise to a helical structure, and the redox results in conformational changes with

chiroptical switching.² Contrastingly, the installation of redox active moieties into a chiral framework is a simple and practical route to design functional molecules exhibiting chiroptical electrochromic properties because a strong and ascertainable chiral exciton coupling of the chromophore can be anticipated during their redox process without large conformational changes. However, the applicable chiral backbone is limited to a 1,1'-binaphthyl skeleton.^{3,4}

An allene framework is so rigid that the axial chirality induces a well-defined chiral relationship between the terminal

(1) Canary, J. W. *Chem. Soc. Rev.* **2009**, 38, 747–756.

(2) (a) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, 374, 790–792. (b) Iida, H.; Mizoguchi, T.; Oh, S.-D.; Yashima, E. *Polym. Chem.* **2010**, 1, 841–848. (c) Goto, H. *J. Mater. Chem.* **2009**, 19, 4914–4921. (d) Zhang, Z.-B.; Fijiki, M.; Motonaga, M.; McKenna, C. E. *J. Am. Chem. Soc.* **2003**, 125, 7878–7881.

(3) (a) Deng, J.; Song, N.; Zhou, Q.; Su, Z. *Org. Lett.* **2007**, 9, 5393–5396. (b) Beer, G.; Niedera, C.; Grimme, S.; Daub, J. *Angew. Chem., Int. Ed.* **2000**, 39, 3252–3255.

(4) (a) Gómez, R.; Segura, L. L.; Martín, N. *Org. Lett.* **2000**, 2, 1585–1587. (b) Gómez, R.; Segura, L. L.; Martín, N. *J. Org. Chem.* **2000**, 65, 7566–7574. (c) Zhou, Y.; Zhang, D.; Zhu, L.; Shuai, Z.; Zhu, D. *J. Org. Chem.* **2006**, 71, 2123–2130.

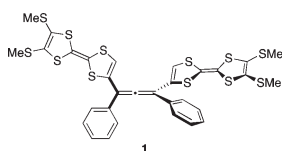
(5) *Modern Allene Chemistry*; Krause, N., Hashimi, A. J., Eds; Wiley-VCH: Weinheim, 2004.

(6) (a) Löhr, S.; Averbeck, J.; Schürmann, M.; Krause, N. *Eur. J. Inorg. Chem.* **2008**, 552–556. (b) Zelder, C.; Krause, N. *Eur. J. Org. Chem.* **2004**, 3968–3971. (c) Janssen, C. E.; Krause, N. *Eur. J. Org. Chem.* **2005**, 2322–2329.

(7) (a) Rivera-Fuentes, P.; Alonso-Gómez, J. L.; Petrovic, A. G.; Santoro, F.; Harada, N.; Berova, N.; Diederich, F. *Angew. Chem., Int. Ed.* **2010**, 49, 2247–2250. (b) Rivera-Fuentes, P.; Alonso-Gómez, J. L.; Petrovic, A. G.; Seiler, P.; Santoro, F.; Harada, N.; Berova, N.; Rzepa, H. R.; Diederich, F. *Chem.—Eur. J.* **2010**, 16, 9796–9807. (c) Rivera-Fuentes, P.; Nieto-Ortega, B.; Schweizer, W. B.; Navarrete, J. T. L.; Casado, J.; Diederich, F. *Chem.—Eur. J.* **2011**, 17, 3876–3885. (d) Alonso-Gómez, J. L.; Rivera-Fuentes, P.; Harada, N.; Berova, N.; Diederich, F. *Angew. Chem., Int. Ed.* **2009**, 48, 5545–5548.

chromophores; hence, chiroptical effects can be generated.^{5–7} We have here designed 1,3-bis(tetrathiafulvalenyl)allene derivative **1** as a new class of electron-donor molecule that is expected to show strong chiroptical properties.

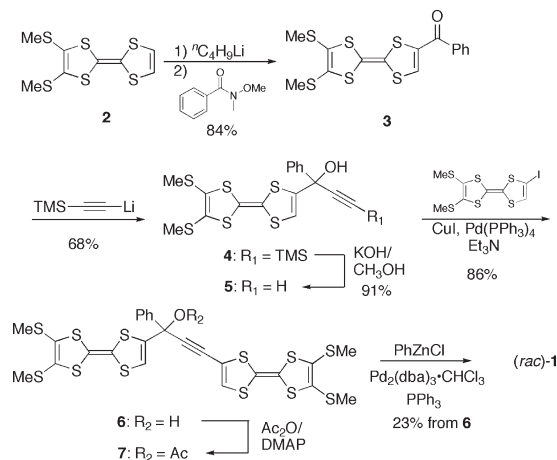
To date, chirality has been introduced into tetrathiafulvalene (TTF)⁸ to observe new phenomena, such as chiral conductors and chiroptical molecular switches,^{9,10} but there are only a few studies on TTF involved in axial chirality, which can be expected to have pronounced chiroptical effects.⁴ Previously, binaphthalene molecules linked by two and four TTF units through long alkyl chains were prepared, and their chiral molecular switching properties were investigated.⁴ In these systems, although the chiral properties were tunable by the addition of oxidants, only small chiroptical effects at high energy region were observed at any oxidation stage, owing to the small chiroptical interactions between their chromophores. Through the direct connection of TTF moieties to an allene backbone with axial chirality, we assume that **1** might exhibit considerably larger chiroptical electrochromic properties over various energy ranges. In this paper, we report the synthesis, structures, optical resolution of the allene, and significant chiroptical electrochromic properties during oxidation.



Novel symmetrical allene **1** was synthesized using palladium-catalyzed S_N2' substitution of propargyl acetate as the key reaction (Scheme 1).^{6a} Propargylic alcohol **6** was easily prepared from 4,5-bis(methylthio)-tetrathiafulvalene **2** in four steps. When **6** was treated with acetic anhydride (Ac_2O) in the presence of *N,N*-dimethyl-4-aminopyridine (DMAP), the corresponding propargylic acetate **7** was formed *in situ*, though the acetate **7** did not prove satisfactorily stable for isolation under ambient conditions. Sequential palladium-catalyzed substitution of **7** with $PhZnCl$ in one pot proceeded to give the expected allene **1** in a 23% yield from **6**. The structure of **1** was characterized by 1H NMR, ^{13}C NMR, DI-MS, IR, and elemental analysis. The chemical shift of the central carbon of **1** in the ^{13}C NMR spectrum was observed at 209.2 ppm,

which is a normal chemical shift for the nonpolarized allene.^{5–7} The IR (1953 cm^{-1} ($\nu_{C=C=C}$)) spectrum also supported the linear structure of the allene moiety of **1**.

Scheme 1. Synthesis of **1**



Single crystals of racemic **1** were obtained by the slow diffusion of methanol into a toluene solution at $4\text{ }^{\circ}\text{C}$, and X-ray analysis was carried out at $-100\text{ }^{\circ}\text{C}$ (Figure 1).¹² The allene skeleton was almost linear ($C1-C2-C3 = 178.17^{\circ}$), and the two TTF moieties were connected orthogonally to each other through the central allene. Each TTF adopted a slight boat conformation and dimerized with the same part of the other enantiomer in the lattice. The shortest intermolecular distance between the atoms and the least-squared plane within the stacked TTFs was found to be $3.39\text{--}3.64\text{ \AA}$, which suggested a significant contact between two intermolecular TTFs through $S\cdots S$ and $\pi\cdots\pi$ interactions. Furthermore, dihedral angles of the TTF groups against the central allene were 5.6 and 18.0° , respectively, whereas those of the two phenyl groups were much larger: 69.2 and 45.8° , respectively. It was thus clear that the two TTFs were conjugated to the central allene more effectively than the phenyl groups.

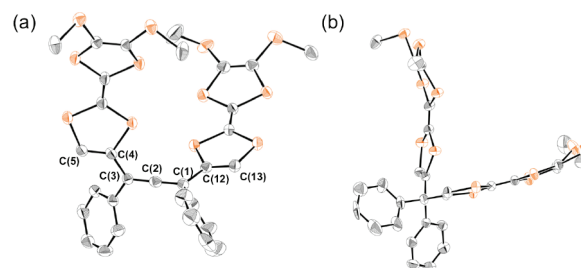


Figure 1. X-ray structure of **1**, (a) top view and (b) side view. Hydrogen atoms are omitted for clarity.

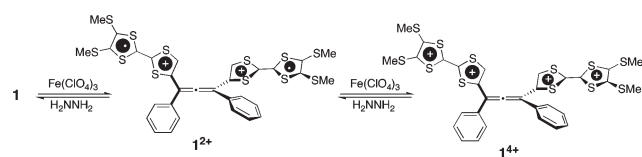
(8) For reviews on tetrathiafulvalene see: (a) *TTF Chemistry: Fundamental and Applications of Tetrathiafulvalene*; Yamada, J., Sugimoto, T., Eds; Kodansha-Springer: Tokyo, 2004. (b) Iyoda, M.; Hasegawa, M.; Miyake, Y. *Chem. Rev.* **2004**, *104*, 5085–5113. (c) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409. (d) Canevet, D.; Sallé, M.; Zhang, G.; Zhu, D. *Chem. Commun.* **2009**, 2245–2269.

(9) (a) Saad, A.; Jeannin, O.; Fourmigué, M. *Tetrahedron* **2011**, *67*, 3820–3829. (b) Danila, I.; Riobe, F.; Piron, F.; Puigmartí-Luis, J.; Wallis, J. D.; Linares, M.; Ágren, H.; Beljonne, D.; Amabilino, D. B.; Avarvari, N. *J. Am. Chem. Soc.* **2011**, *133*, 8344–8353. (c) Wallis, J. D.; Griffiths, J.-P. *J. Mater. Chem.* **2005**, *15*, 347–365. (d) Matsumiya, S.; Izuoka, A.; Sugawara, T.; Taruishi, T.; Kawada, Y.; Tokumoto, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1949–1954. (e) Réthoré, C.; Avarvari, N.; Canadell, E.; Auban-Senzier, P.; Fourmigué, M. *J. Am. Chem. Soc.* **2005**, *127*, 5748–5749. (f) Rikken, G. L. J. A.; Fölling, J.; Myder, P. *Phys. Rev. Lett.* **2001**, *87*, 236602–236605.

(10) Gomar-Nadal, E.; Jaume, V.; Rovira, C.; Amabilino, D. B. *Adv. Mater.* **2005**, *17*, 2095–2098.

The cyclic voltammogram (CV) of **1** (1.0×10^{-3} M in PhCN) showed two reversible redox waves assigned to TTF/TTF^{•+} and TTF^{•+}/TTF²⁺ at 0.06 and 0.40 V (vs Fc/Fc⁺), which were similar to those of **2** (0.03 and 0.35 V under similar conditions).¹³ Because the allene **1** possesses a good donor ability, chemical oxidation affords the oxidized TTF species (Scheme 2). In fact, treatment of **1** with 2 and 6 equiv. of Fe(ClO₄)₃ in CH₂Cl₂-MeCN (v/v = 4:1) gave **1**²⁺ and **1**⁴⁺, which were comparable to **2**^{•+} and **2**²⁺, respectively (Figure 2). During the sequential addition of Fe(ClO₄)₃ up to 2 equiv to **1**, only one phase changed while the same isosbestic points were observed.¹¹ This behavior clearly indicated that there was no intramolecular electronic interaction between the two TTF units in **1**²⁺.

Scheme 2. Chemical Oxidation of **1**



In the electronic spectrum of **1**²⁺, the absorption maximum was found at 790 nm, which was typically assigned to an absorption band derived from an electron transition to the SOMO in TTF^{•+}, while the absorption maxima of **2**^{•+} under similar conditions was observed at 744 nm.¹⁴ Such significant red-shift of **1**²⁺ was due to the effective conjugation of the TTF units and the central allene moieties. Similarly for the tetracation **1**⁴⁺, the absorption maximum of 652 nm, which is typically assigned to the HOMO–LUMO transition in TTF²⁺ moieties, was also red-shifted compared with the corresponding peak in **2**²⁺ ($\lambda_{\text{max}} = 622$ nm).¹⁴ In addition, neutral **1** was recovered without significant decomposition when these cationic species were treated with excess H₂NNH₂·H₂O.

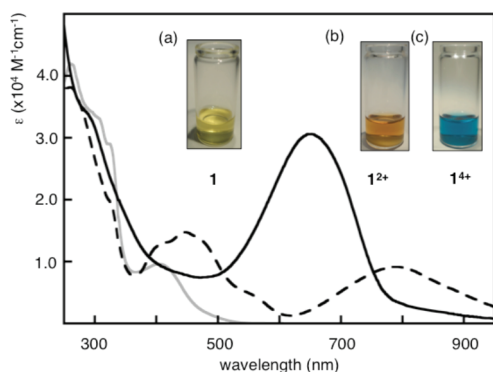


Figure 2. Electronic spectra and the colors of **1** (solid gray line), **1**²⁺ (dash line), and **1**⁴⁺ (solid black line) in CH₂Cl₂-MeCN (v/v = 4:1) solution.

Since strong chiroptical effects between the TTF moieties of optically active **1** were anticipated, we carried out optical resolution of racemic **1** by chiral HPLC (DAICEL chiralpak IA-3). Elution of *rac*-**1** with CHCl₃-hexane-EtOH solution (v/v = 10:40:0.2) afforded optically pure (+)-**1** and (–)-**1**, whose optical rotations ($[\alpha]_D^{24}$ in CH₂Cl₂) were +760 and –760°, respectively.¹¹ The electronic circular dichroism (ECD) spectra of the allenes (+)-**1** and (–)-**1** were measured in CH₂Cl₂ solution and are depicted in Figure 3. Both of the ECD spectra showed strong Cotton Effects over their entire absorption range, and they possessed distinctive bisignate bands at 280 and 335 nm together with shoulder band tails up to approximately 540 nm. Because the absorption spectrum of **1** extended into the long wavelength region up to 550 nm, the observed Cotton Effects in the visible region were associated with the transition of the TTF moieties.

To assign the absolute configuration of the optically active allene and to study the origin of the observed Cotton Effects, the electronic transition energies and the rotational strengths were calculated with time-dependent (TD) DFT calculations after geometry optimization at the B3LYP/6-31G(d,p) level.¹⁵ The optimized molecular geometry of **1**, with C₂ symmetry, was close to the structure obtained from X-ray analysis. As shown in Figure 3, TD-DFT calculation of the optimized structure of (*S*)-**1** provided a reproduction of the features of the qualitative ECD spectrum experimentally obtained from the (+)-allene isomer. Therefore, we assumed that the (+)-**1** obtained from the chiral HPLC separation should have the (*S*) configuration. The simulated spectrum of (*R*)-**1** was also attributed to a mirror spectrum opposite to (*S*)-**1**, and hence the (–)-allene isomer should have the (*R*) configuration.¹¹ The TD-DFT calculation of (*S*)-**1** revealed that the positive rotational strengths at lower energy (S₁, S₂, and S₃ in Figure 3) were related to the transition of the TTF moieties. Thus, the direct connection of two TTFs to the allene induced strong chiroptical properties, as evidenced in the ECD spectra.

Although the internal rotation barrier of the allenic C=C=C axis is generally large ($\Delta G^\ddagger = 46$ kcal/mol for

(12) Crystal data for **1**: C₃₁H₂₄S₁₂·1.5(C₇H₈), *M_w* = 918.92, red block, triclinic, space group P1 (#2), *a* = 9.9898(7), *b* = 14.5484(10), *c* = 15.5784(10) Å, α = 93.462(1), β = 94.603(1), γ = 101.437(1)°, *V* = 2205.2(3) Å³, *Z* = 2, *D_c* = 1.384 g cm^{–3}, 173 K, μ = 0.624 mm^{–1}, 12 441 reflections measured, 9472 unique (*R_{int}* = 0.0131), final *R* indices [*I* > 2σ(*I*)]: *R*₁ = 0.0394, *wR*₂ = 0.1046, GOF = 1.035.

(13) The CV analysis was carried out in PhCN solution with 0.1 M *n*-Bu₄NClO₄ as a supporting electrolyte at 23 °C using Pt working and counter electrodes. The potentials were measured against Ag/Ag⁺ and converted to Fc/Fc⁺.

(11) See Supporting Information.

(14) (a) Nakamura, K.-I.; Takashima, T.; Shirahata, T.; Hino, S.; Hasegawa, M.; Mazaki, Y.; Misaki, Y. *Org. Lett.* **2011**, *13*, 3122–3125. (b) Iyoda, M.; Hasegawa, M.; Kuwatani, Y.; Nishikawa, H.; Fukami, K.; Nagase, S.; Yamamoto, G. *Chem. Lett.* **2001**, 1146–1147.

(15) Frisch, M. J.; et al. *Gaussian 09*, Revision B.01; Gaussian Inc.: Pittsburgh, PA, 2009.

(16) (a) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48–52. (b) *Dynamic Stereochemistry of Chiral Compounds*; Wolf, C., Ed.; RSC Publishing: Cambridge, 2008.

(17) (a) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971–3980. (b) Alonso-Gómez, J. L.; Schanen, P.; Rivera-Fuentes, P.; Seiler, P.; Diederich, F. *Chem.—Eur. J.* **2008**, *14*, 10564–10568.

1,3-dialkylallenes),¹⁶ some allenes having electron donating groups are susceptible to photoracemization in a solution.^{16b,17} In our system, the optically pure allene **1** was gradually racemized in solution at rt without chemical decomposition. The racemization of **1** in solution showed a good relationship in the first-order rate plot.¹¹ The half-lives of (+)-**1** in CH₂Cl₂ and CH₂Cl₂-MeCN (v/v = 4:1) solution (5.1×10^{-5} M), obtained from the analysis of the ellipticity changes at 281 nm, were 56 and 76 min, respectively. Whereas the ellipticity decreased during daylight, no racemization was observed in solution in the dark or stored in amber glassware.¹⁸

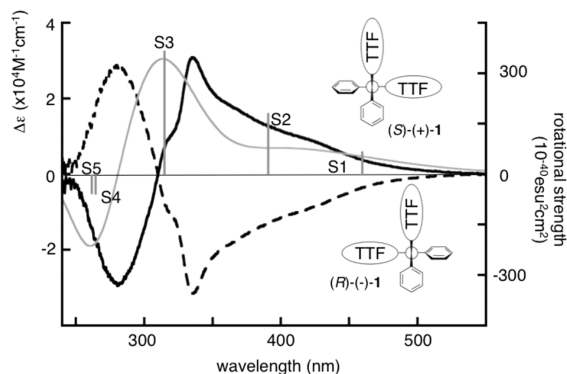


Figure 3. ECD spectra of (S)-(+)-**1** (solid black line), (R)-(-)-**1** (dash line) in CH₂Cl₂, the simulated ECD spectrum of (S)-**1** (gray line), and the selected rotational strength (gray bar) at TD-DFT (B3LYP/6-31G(d,p)) calculated for 64 states.

Because the photoracemization is slow enough in CH₂Cl₂-MeCN solution, we carried out the chemical oxidation of optically pure allene **1** with Fe(ClO₄)₃.¹⁸ As shown in the ECD spectra of **1**²⁺ (Figure 4), strong Cotton Effects were observed over almost the whole visible region. For example, CD spectrum of (S)-**1**²⁺ displayed a broad positive band at low energy with a maximum at approximately 800 nm, a bisignate signal in the 330–620 nm region, and a strong negative sign with maximum at 293 nm. Meanwhile, the ECD spectrum of (R)-**1**²⁺ was its mirror image. Since the longest wavelength absorption of **1**²⁺ was assigned to the electron transition of the TTF^{•+} moiety, the observed negative/positive sign in the ECD spectrum was a result of the strong chiroptical nature of the allene. In particular, each optically pure **1**²⁺ notably exhibited only negative/positive molar ellipticity over the range 445–1000 nm.

The ECD spectra of tetracation **1**⁴⁺ were also found to be quite different from those of **1**²⁺ (Figure 4). A pair of very intense Cotton Effects ($\lambda_{\text{ex}} = 704$ and 600 nm) in the region of the HOMO–LUMO transition ($\lambda_{\text{max}} = 652$ nm) was observed together with relatively weak bisignate signals at high energy with maxima at 378 and 330 nm (Figure 4). Since the intense couplet at low energy possessed a typical

exciton-type signal shape, unlike the ECD spectrum of the dication, a very strong exciton coupling whose transition moments were localized at the terminal TTF²⁺ moieties was induced by the axial chirality.

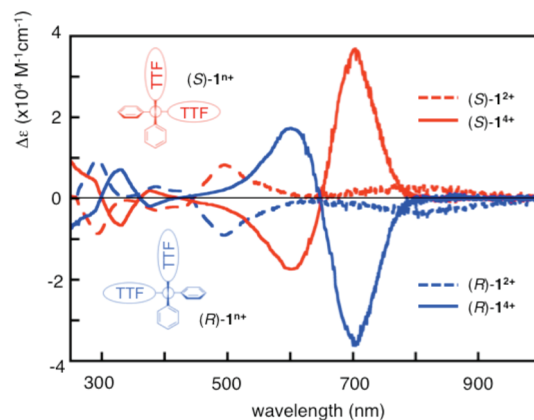


Figure 4. ECD spectra of (S)-**1**²⁺ (dash red line), (S)-**1**⁴⁺ (solid red line), (R)-**1**²⁺ (dash blue line), and (R)-**1**⁴⁺ (solid blue line) in CH₂Cl₂-MeCN (v/v = 4:1) solution. A low S/N ratio on the spectra at lower energy was an instrumental artifact.

In summary, we have designed and synthesized a novel chiral allene (**1**) that has TTF moieties as electron donors, and we have succeeded in the optical resolution of **1** into its enantiomers, whose absolute configurations were validated by TD-DFT calculations. As expected, both of the optically pure allenes exhibited strong chiroptical properties. The chemical oxidation of these optically pure allenes resulted in different Cotton Effects in their ECD spectra depending on the oxidation stage of the TTF units. These results indicated that a wide range of intensely chiroptical electrochromic properties could be realized by controlling the oxidation of the TTF moieties. We believe that the present redox-active allene provides a new class of chiroptical electrochromic materials.

Acknowledgment. We are grateful to Prof. Kazumasa Kajiyama (Kitasato University) and Mr. Ken-ichiro Miyazawa (Daicel Chemical Industries, Ltd.) for helpful advice on optical resolution, the Interdisciplinary Laboratory for Nanoscale Science and Technology in NIMS for measurements of ECD spectra, Dr. Yoshihiro Miyake (University of the Tokyo) for helpful discussion, and Prof. Mao Minoura (Kitasato University) for valuable advice on X-ray crystallographic analysis. This work was partially financial supported by a Daicel Chemical Industry Award in The Society of Synthetic Organic Chemistry, Japan, and by Kitasato University Research Grant for young researchers.

Supporting Information Available. Detailed experimental procedures and characterization data for new compounds, HPLC chromatograms, photoracemization details for **1**, DFT molecular coordinates of **1**, and full reference of 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(18) The manipulation for the measurements of ECD treated under the dark. The chemical oxidation was carried out in amber glassware. As for the racemization under light, further studies of the kinetics and mechanism using an arc lamp are currently underway.