

Photochromic Performance of 1-Thiazolyl-2-vinylcyclopentene Derivatives Having a Phenyl- or 4-Methoxyphenyl-Substituted Olefin

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1-Thiazolyl-2-vinylcyclopentene derivatives, 1-(5-methoxy-2-phenyl-4-thiazolyl)-2-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene (**1a**), 1-[5-methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene (**2a**), and 1-[5-methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-[1-(4-methoxyphenyl)-2-methyl-1-propenyl]perfluorocyclopentene (**3a**) were synthesized in an attempt to obtain yellow photochromic compounds having low photocycloreversion quantum yields and large absorption coefficients of the closed-ring isomers. Their photochromic performance, thermal stability, and fatigue resistance were compared with 1-[5-methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-(1,2-dimethyl-1-propenyl)perfluorocyclopentene (**4a**) having a methyl-substituted olefin. Upon irradiation with 313 nm light, compounds **1a**, **2a**, and **3a** changed from colorless to various shades of yellow in toluene. The conversions from the open-ring (**1a**, **2a**, and **3a**) to the closed-ring (**1b**, **2b**, and **3b**) isomers in the photostationary state under irradiation with 313 nm light were 93, 95, and 98%, respectively. Among the three derivatives **3b** has the largest absorption coefficient ($\varepsilon = 18900\,M^{-1}\,cm^{-1}$) at 428 nm and the lowest cycloreversion quantum yield of 1.8×10^{-3}.

Photochromic compounds have attracted much attention because of their potential applications to optical memory, photooptical switching, and display devices.[1] In particular, diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene groups, are the most promising candidates for the applications, because they undergo fatigue resistant and thermally irreversible photochromic reactions.[2] For the application to a full color display preparation of yellow developing photochromic compounds which have low photocycloreversion quantum yields and thermal stability at room temperature is indispensable. Although some photochromic compounds exhibit yellow color, the colored isomers are photochemically unstable and the photocycloreversion quantum yields are rather high.[3] Recently, 1-heteroaryl-2-vinylcyclopentene derivatives having a thiophene ring and a 2-butene or styryl unit have been reported by Peters et al.[4] and Yokoyama et al.[5] The colorless solutions of these compounds turn yellow by irradiation with UV light.

In a previous paper,[6] we have also prepared 1-heteroaryl-2-vinylcyclopentene derivative **4a** with a thiazole ring. The closed-ring isomer of **4a** having two methoxy groups shows the absorption maximum at 416 nm ($\varepsilon = 17100\,M^{-1}\,cm^{-1}$) in toluene and a photocycloreversion quantum yield of 0.0014.[6] The methoxy substituents effectively decrease the photocycloreversion quantum yield[7] and induce the large absorption coefficient of the closed-ring isomer.[8] The derivative is a useful candidate as a yellow developing photochromic dye. Although the photochromic performance of these 1-heteroaryl-2-vinylcyclopentene derivatives is of great interest, their fatigue resistance is limited because of the formation of by-products.[4–6,9] In this study, we have synthesized three 1-thiazolyl-2-vinylcyclopentene derivatives **1a**, **2a**, and **3a** by introducing a phenyl- or 4-methoxyphenyl-substituted olefin to know the relationship between the structure and the photochromic performance, as shown in Scheme 1. The absorption maxima of closed-ring isomers **1b**–**3b** are expected to show a bathochromic shift. In other words, the closed-ring isomers **1b**–**3b** are able to provide various shades of yellow. Thermal stability of the closed-ring isomers and the fatigue resistance have also been studied in detail.

Results and Discussion

Synthesis of 1-Thiazolyl-2-vinylcyclopentene Derivatives. Compounds **1a** and **2a** were synthesized by the reaction of 4-bromo-5-methoxy-2-phenylthiazole (**5**)[10] or 4-bromo-5-methoxy-2-(4-methoxyphenyl)thiazole (**6**)[6] with 1-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene,[5a] respectively, by bromine–lithium exchange followed by the nucleophilic displacement of fluoride (Scheme 2). Both compounds were obtained in 22 and 18% yields, respectively. Compound **3a** was also synthesized by the reaction of 1-bromo-2-methyl-1-(4-methoxyphenyl)propene (**10**) with 1-[5-methoxy-2-(4-methoxyphenyl)]perfluorocyclopentene[6] by bromine–lithium exchange followed by the nucleophilic displacement of fluoride

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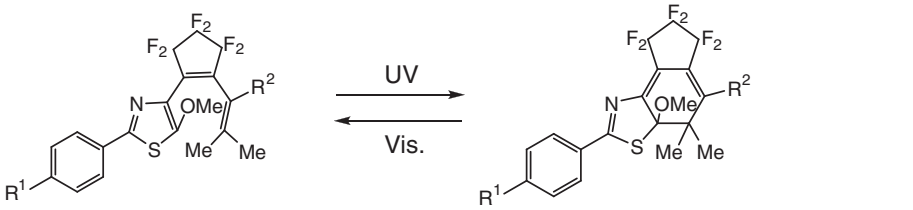
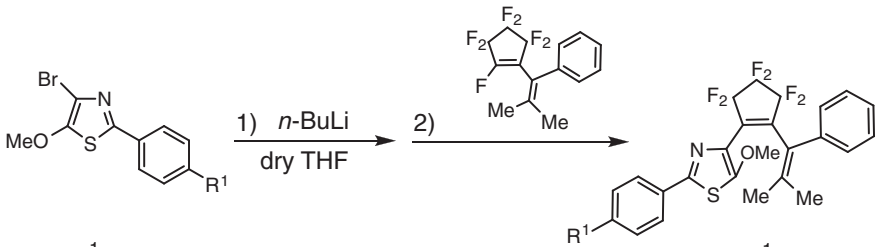


1a : R^1 = H, R^2 = Ph
2a : R^1 = OMe, R^2 = Ph
3a : R^1 = OMe, R^2 = (4-MeO)C_6H_4
4a: R^1 = OMe, R^2 = Me

1b : R^1 = H, R^2 = Ph
2b : R^1 = OMe, R^2 = Ph
3b : R^1 = OMe, R^2 = (4-MeO)C_6H_4
4b: R^1 = OMe, R^2 = Me

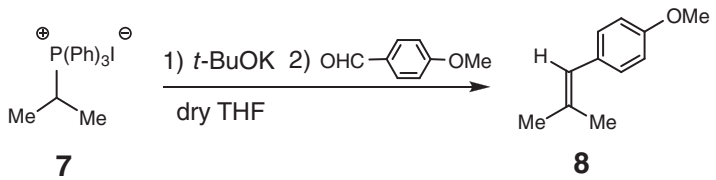
Scheme 1.



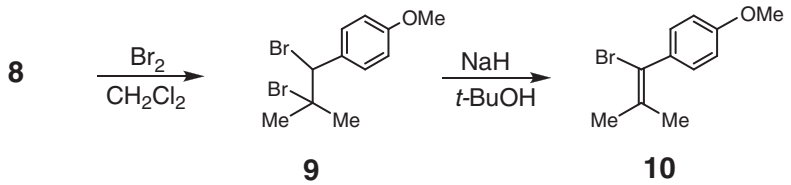
5 : R^1 = H
6 : R^1 = OMe

1a : R^1 = H
2a : R^1 = OMe

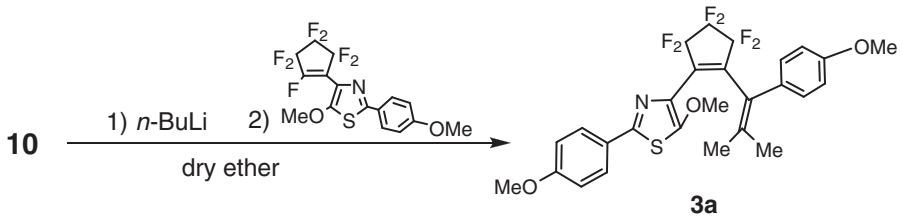
Scheme 2.



7 **8**



9 **10**



3a

Scheme 3.

(Scheme 3). A colorless solid was obtained in 36% yield. The synthesis of compound **8** was carried out by the Wittig reaction from isopropyltriphenylphosphonium iodide (**7**) and *p*-anisaldehyde in 85% yields. Compounds **1a**, **2a**, and **3a** were purified by column chromatography (hexane/AcOEt) and characterized by ^{1}H NMR spectroscopy, MS, and elemental analysis.

Absorption Spectra and Quantum Yields. Figure 1 shows the absorption spectral change of **1** (2.95×10^{-5} M) in toluene by irradiation with UV light. The spectrum of the isolated closed-ring isomer is also shown in Figure 1. Upon irradiation with 313 nm light the colorless toluene solution of **1a** slowly turned pale yellow, in which the absorption maximum was observed at 419 nm ($\varepsilon = 12500\,M^{-1}\,cm^{-1}$). When the pale yellow solution was irradiated with visible light ($\lambda >$ 440 nm), the spectrum readily returned back to colorless one. The pale yellow color is due to the closed-ring isomer **1b**. In a

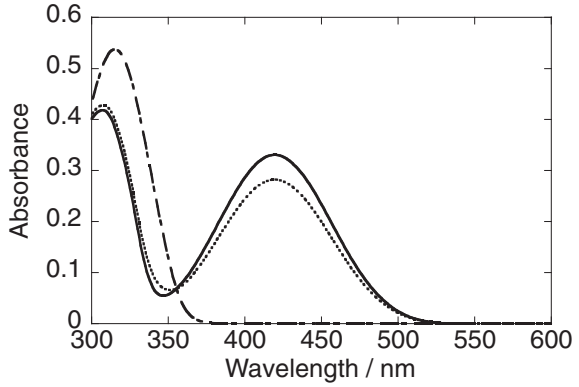


Figure 1. Absorption spectra of compound **1** (2.95×10^{-5} M) in toluene: (dashed line) open-ring isomer **1a**, (solid line) closed-ring isomer **1b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

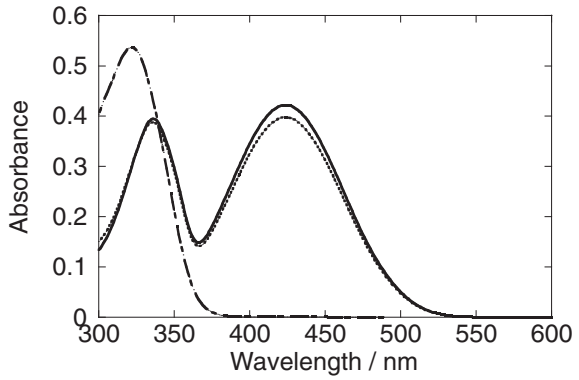


Figure 2. Absorption spectra of compound **2** (2.43×10^{-5} M) in toluene: (dashed line) open-ring isomer **2a**, (solid line) closed-ring isomer **2b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

previous paper,[9] it was reported that 1-thiazolyl-2-vinylcyclopentene having a methyl group at 5-position of the thiazole ring forms a by-product upon UV irradiation. When the methyl group was substituted with a methoxy group, the by-product formation was suppressed. This indicates that the methoxy substituent at the 5-position is indispensable for the molecule to undergo reversible photochromic reactions. The colored closed-ring isomer was stable in the dark at room temperature and could be isolated by high-performance liquid chromatography (HPLC, silica gel column, hexane/ethyl acetate = 80:20). The conversion from **1a** to **1b** in the photostationary state under irradiation with 313 nm light was 93%.

Figure 2 shows the absorption spectral changes of **2** (2.43×10^{-5} M) in toluene by UV irradiation. The colorless solution turned yellow upon irradiation with 313 nm light and a new absorption band appeared at 424 nm. The yellow color is due to the closed-ring isomer **2b** and bleached by irradiation with visible light ($\lambda > 440$ nm). The absorption coefficient of **2b** was determined to be 17400 M^{-1} cm^{-1}, which is larger than that of **1b**. The conversion from the open-ring to the closed-ring isomer by irradiation with 313 nm was 95%. The photocyclization/cycloreversion quantum yields were determined in toluene at 25 °C. The photocyclization quantum yields were

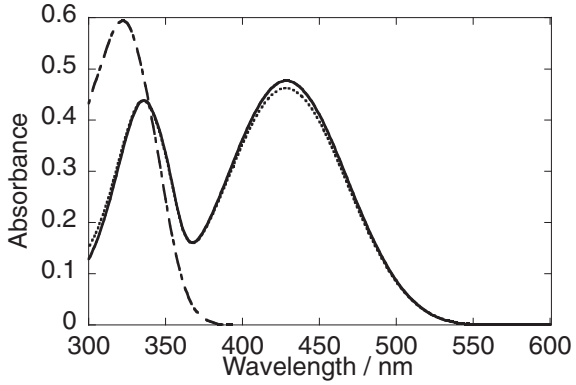


Figure 3. Absorption spectra of compound **3** (2.52×10^{-5} M) in toluene: (dashed line) open-ring isomer **3a**, (solid line) closed-ring isomer **3b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

measured by irradiation with 313 nm light, while the photocycloreversion quantum yields were measured by irradiation with 416 nm light. The photocyclization quantum yields of **1a** and **2a** were 0.15 and 0.20, respectively. The photocycloreversion quantum yields of **1b** and **2b** were 7.8×10^{-3} and 4.2×10^{-3}, respectively. The photocycloreversion quantum yield of **2b** was a half of that of **1b**. The decrease is ascribed to the introduction of the methoxy substituent at the *para*-position of the phenyl ring.[8]

Figure 3 shows the absorption spectral changes of **3** (2.52×10^{-5} M) in toluene by UV irradiation. Similar color and spectral changes were observed. The absorption maximum (428 nm) is 9 nm longer than that of **1b** (419 nm) in toluene and the solution shows a slightly deep yellow color. The yellow color was bleached by irradiation with visible light ($\lambda > 440$ nm). The photobleaching rate of **3b** was slower than that of **1b** and **2b**. The conversion from the open-ring to the closed-ring isomers by irradiation with 313 nm was 98%. The absorption coefficient of the closed-ring isomer **3b**, (18900 M^{-1} cm^{-1}), is 1.5 times larger than that of **1b**. Introduction of a 4-methoxyphenyl-substituted olefin is effective in increasing the ε value of the closed-ring isomer.

Table 1 summarizes the photocyclization and photocycloreversion quantum yields of **1**–**4**. The photocyclization quantum yields of these four derivatives **1**–**4** are similar in the range from 0.15 to 0.19. On the other hand, the photocycloreversion quantum yield was found to increase by replacing the methyl group at R^2 with phenyl substituents. The cycloreversion quantum yield of **1b** (7.8×10^{-3}) is 5 times larger than that of **4b** (1.4×10^{-3}). The cycloreversion quantum yields of **3b** (1.8×10^{-3}) and **4b** are almost the same. Figure 4 shows the photos of the color changes of four derivatives **1**–**4** upon UV irradiation. When the toluene solutions of the derivatives **1a**–**4a** are irradiated with UV light, these colorless solutions turn to various shade of yellow. As can be seen in Figure 4, the four derivatives exhibit yellow colors from pale to golden deep yellow.

Thermal Stability and Fatigue Resistance. The thermal stability of the closed-ring isomers and the fatigue resistance of compounds **1**–**4** were measured, as shown in Figures 5 and 6. Figure 5 shows the thermal stability of the closed-ring isomers

Table 1. Absorption Maxima and Coefficients of the Open- and Closed-Ring Isomers of Compounds **1**, **2**, **3**, and **4**, and the Quantum Yields in Toluene

	λ_{max} /nm (ε/M^{-1} cm^{-1})	$\Phi_{a\rightarrow b}$		λ_{max} /nm (ε/M^{-1} cm^{-1})	$\Phi_{b\rightarrow a}$	Conversion
1a	316 (20210)	0.15 (313 nm)	**1b**	419 (12500)	7.8×10^{-3} (416 nm)	0.93
2a	322 (22100)	0.20 (313 nm)	**2b**	424 (17400)	4.2×10^{-3} (416 nm)	0.95
3a	322 (23600)	0.17 (313 nm)	**3b**	428 (18900)	1.8×10^{-3} (416 nm)	0.98
4a	320 (22100)	0.19 (313 nm)	**4b**	416 (17100)	1.4×10^{-3} (416 nm)	0.97[a)]

a) Ref. 6.

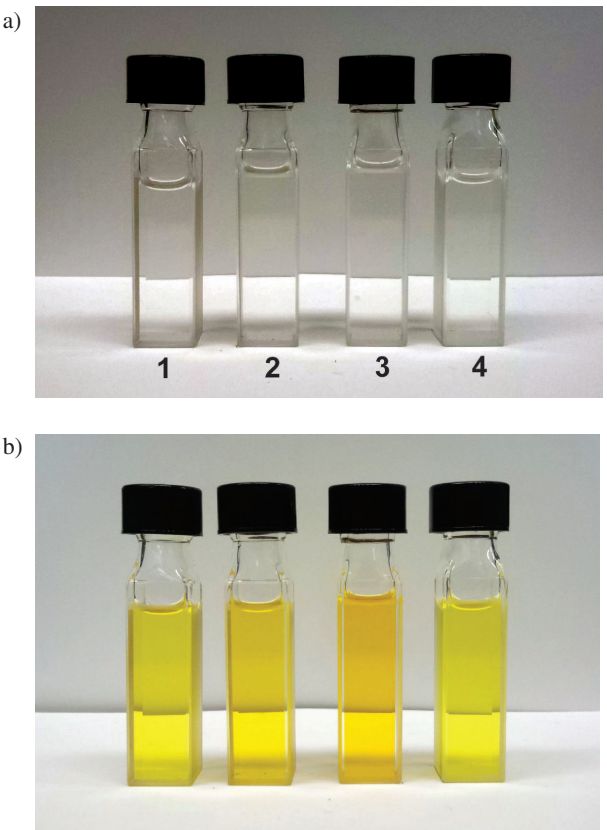


Figure 4. Photographs of color changes of compounds **1**, **2**, **3**, and **4** under irradiation with 313 nm in toluene: a) before photoirradiation, b) after photoirradiation.

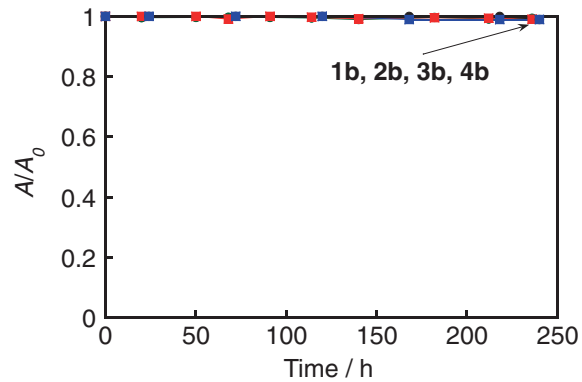


Figure 5. Thermal stability of the closed-ring isomers **1b** (black circles), **2b** (blue squares), **3b** (green circles), and **4b** (red squares) in toluene.

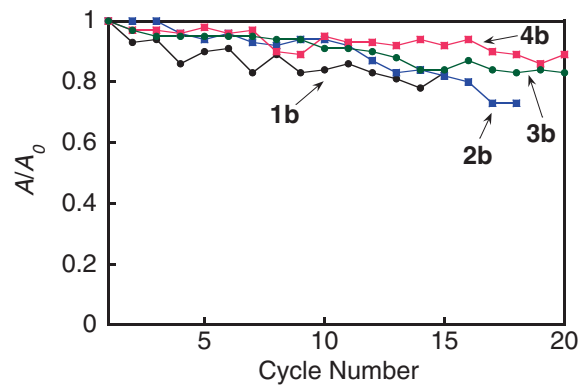


Figure 6. Fatigue-resistance of compounds **1** (black circles), **2** (blue squares), **3** (green circles), and **4** (red squares) in toluene. Absorbances of **1b**–**4b** were plotted after irradiation with UV light.

1b, **2b**, **3b**, and **4b** in toluene at 80 °C in the dark. The value of A/A_0 was plotted against the storage time in the dark, where A_0 is the initial absorbance and A the absorbance after t hours at 80 °C. As can be seen from Figure 5, the absorbances of the photogenerated closed-ring isomers **1b**, **2b**, **3b**, and **4b** remain constant for 100 h. Even after 240 h storage no appreciable decrease of the absorbances was observed.

Fatigue resistance, the number of times that photocyclization and cycloreversion reactions can be repeated without loss of performance, is indispensable for practical applications. According to the method described in the reference,[11] fatigue resistance of compounds **1**–**4** was measured. Toluene solutions of compounds **1**, **2**, **3**, and **4** were irradiated at first with UV light (300–400 nm) and then bleached with visible light ($\lambda >$ 440 nm). The absorption intensity changes at the wavelength of λ_{max} of the closed-ring isomers was followed against the coloration/decoloration cycles, as shown in Figure 6. The toluene solution of **3a** (absorbance was about 0.6 at $\lambda_{max} = 322$ nm) was irradiated with UV light (300–400 nm) for 13 s and then with visible light for more than 12 min in the absence of air. The absorbances of **1b**–**4b** show gradual decrease in 30 cycles. Among the three compounds **3** showed superior fatigue resistance and was comparable to that of **4**.

The conversion of open-ring isomer **1a** to closed-ring isomer **1b** was also followed using ^{1}H NMR spectroscopy, as shown in Supplementary Figure 1. In the ^{1}H NMR spectrum of **1a** in $CDCl_3$, the signals of the methoxy group and the two methyl groups were observed at $\delta = 4.05$ and 1.77 and 1.65 ppm, respectively. Upon irradiation with UV light (300–400 nm) for 10 min, these signals decreased in intensity, while new peaks

appeared at 3.30 and 1.47 and 1.16 ppm. These new peaks are assigned to those of closed-ring isomer **1b**. In addition to these, several additional weak new peaks (such as $\delta = 4.02$ and 3.40 and 1.68 ppm) also appeared. These additional signals did not decrease upon irradiation with visible light ($\lambda > 440$ nm) and were assigned to by-products,[4,5] though the chemical structures were not specified. On the other hand, such additional signals were not observed in the ^{1}H NMR spectrum of **3a** upon irradiation with UV light (300–400 nm) for 10 min. This result also shows that compound **3** has superior fatigue resistance.

Conclusion

We have examined the photochromic performance of 1-thiazolyl-2-vinylcyclopentene derivatives **1a**–**3a** bearing a phenyl- or 4-methoxyphenyl-substituted olefin. When the methyl group at the 5-position of the thiazole ring was replaced with a methoxy group, the by-product formation was suppressed and reversible photochromic reactions were observed. Upon irradiation with 313 nm light, the colorless toluene solutions of **1a**, **2a**, and **3a** turned to various tone of yellow. The absorption maxima of **1b** (419 nm), **2b** (424 nm), and **3b** (428 nm) showed bathochromic shift as much as 3–12 nm relative to the maximum of **4b** (416 nm). Among the three compounds **3** has the highest absorption coefficient of the closed-ring isomer **3b** (18900 M^{-1} cm^{-1}) and exhibits superior fatigue resistance. The closed-ring isomers **1b**–**3b** were found to be thermally stable at 80 °C for more than 240 h.

General. ^{1}H NMR spectra were recorded on a JEOL JMN-ECP 400 (400 MHz) instrument. Mass spectra were measured with a Perkin-Elmer Turbo Mass gas chromatography-mass spectrometer and a Shimadzu GCMS-PARVUM2 gas chromatography-mass spectrometer. High-resolution mass spectra (HRMS) were obtained with a JEOL MS-700. Absorption spectra were recorded on a Shimadzu UV-1800 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W super high-pressure mercury lamp or an Ushio 500 W xenon lamp. Monochromatic light was isolated by passing the light through a cutoff filter (UV-27) and monochromator (SPG-120S, Shimadzu). Elemental analyses were performed by the Laboratory for Organic Elemental Microanalysis, Kyoto University. The cyclization quantum yields were determined by comparing the photocyclization rate of furyl flugide in toluene with a standard procedure. The cycloreversion quantum yields were measured using **4** in toluene as a reference.

Materials. Compounds **5**,[10] **6**,[6] 1-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene,[5a] and 1-[5-methoxy-2-(4-methoxyphenyl)]perfluorocyclopentene[6] were prepared according to methods reported previously. Spectroscopic grade solvents were purified by distillation before use. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Kagaku 63–201 μm).

Synthesis of 1-(5-Methoxy-2-phenyl-4-thiazolyl)-2-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene (1a). To a stirring solution of 4-bromo-5-methoxy-2-phenylthiazole (**5**)[10] (500 mg, 1.85 mmol) in dry THF (10 mL) was slowly added 1.6 M *n*-BuLi in hexane (1.21 mL, 1.94 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 15 min at −80 °C, 1-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene[5a] (900 mg, 2.78 mmol) in dry THF (1 mL) was added. The reaction mixture was further stirred at −80 °C for 2 h, and then distilled water was added. The product was extracted with ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 2/8) to afford to 202 mg (22%) of **1a** as solid: mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.74 (m, 2H), 7.40–7.22 (m, 8H), 4.05 (s, 3H), 1.77 (s, 3H), 1.65 (s, 3H); MS *m/z* 495 [M^+]. Calcd for $C_{25}H_{19}F_6NOS$: C, 60.60; H, 3.87; N, 2.83%. Found: C, 60.49; H, 3.88; N, 2.76%.

Synthesis of 1-[5-Methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene (2a). To a stirring solution of 4-bromo-5-methoxy-2-(4-methoxyphenyl)thiazole (**6**)[6] (500 mg, 1.67 mmol) in dry THF (10 mL) was slowly added 1.6 M *n*-BuLi in hexane (1.10 mL, 1.76 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 15 min at −95 °C, 1-(2-methyl-1-phenyl-1-propenyl)perfluorocyclopentene[5a] (773 mg, 2.38 mmol) in dry THF (1 mL) was added. The reaction mixture was further stirred at −80 °C for 2 h, and then distilled water was added. The product was extracted with ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 2/8) to afford to 158 mg (18%) of **2a** as solid: mp 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, $J = 8.8$ Hz, 2H), 7.35–7.22 (m, 5H), 6.88 (d, $J = 8.8$ Hz, 2H), 4.01 (s, 3H), 3.82 (s, 3H), 1.75 (s, 3H), 1.63 (s, 3H); MS *m/z* 525 [M^+]. Calcd for $C_{26}H_{21}F_6NO_2S$: C, 59.42; H, 4.03; N, 2.67%. Found: C, 59.72; H, 3.83; N, 2.37%.

Synthesis of Isopropyltriphenylphosphonium Iodide (7). A solution of 2-iodopropane (35 g, 204 mmol) and triphenylphosphine (53 g, 203 mmol) in acetonitrile (325 mL) was refluxed for 5 days. The solution was allowed to cool to room temperature. After evaporation of the solvent, the residue was washed with ether three times to afford 75 g (85%) of **7** as pale yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0–7.9 (m, 6H), 7.8–7.65 (m, 9H), 5.35–5.25 (m, 1H), 1.35 (d, $J = 7.0$ Hz, 3H), 1.30 (d, $J = 7.0$ Hz, 3H), Calcd for $C_{21}H_{22}IP$: C, 58.35; H, 5.13%. Found: C, 58.05; H, 5.13%.

Synthesis of 2-Methyl-1-(4-methoxyphenyl)-1-propene (8). To a solution of **7** (25 g, 58 mmol) in dry THF (230 mL) was added slowly 1 M potassium *tert*-butoxide (58 mL, 58 mmol) in THF at room temperature under argon. After the mixture was stirred for 30 min at room temperature, *p*-anisaldehyde (3.30 g, 24 mmol) in dry THF (40 mL) was added. The reaction mixture was further stirred for 12 h and then distilled water was added. The product was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1/9) to afford 3.57 g (95%) of **8** as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.20 (s, 1H), 3.78 (s, 3H), 1.87 (s, 3H), 1.84 (s, 3H), MS (GC) *m/z* 163 ([M + 1]: 11%), 162 (M: 100%), 147 ([M − CH_3]: 92%). Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%. Found: C, 81.58; H, 8.99%.

Synthesis of 1-(1,2-Dibromo-2-methylpropyl)-4-methoxybenzene (9). To a solution of **8** (1.20 g, 7.4 mmol) in dichloromethane (40 mL) was added bromine (1.16 g, 7.3 mmol)

in dichloromethane (8 mL) at −80 °C, and stirring was continued for 30 min at the same temperature. To the reaction mixture was added aqueous sodium thiosulfate. The mixture was extracted with dichloromethane, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (AcOEt/hexane = 1/9) to afford 1.37 g (58%) of **9** as colorless oil (This compound **9** is unstable): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.25 (s, 1H), 3.82 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H); MS (GC): m/z 243 ([M − ^{80}Br]: 24%), 241 ([M − ^{82}Br]: 25%), 162 ([M − 2Br]: 100%), 147 ([M − 2Br − CH_3]: 76%).

Synthesis of 1-Bromo-1-(4-methoxyphenyl)-2-methyl-1-propene (10). To a solution of **9** (1.37 g, 4.28 mmol) in *t*-butyl alcohol (9 mL) was added sodium hydride (40% in mineral oil, 154 mg, 6.42 mmol, 1.5 equiv) and the resulting mixture was stirred for 20 h at 40 °C. After adding water, the mixture was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (AcOEt/hexane = 1/9) to afford 760 mg (74%) of **10** as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H). MS (GC): m/z 242 (M: 23%), 240 (M: 23%), 161 ([M − Br]: 100%), 91 ([M − Br − CH_3]: 29%). Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43%. Found: C, 54.94; H, 5.46%.

Synthesis of 1-[5-Methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-[2-methyl-1-(4-methoxyphenyl)-1-propenyl]perfluorocyclopentene (3a). To a stirring solution of **10** (220 mg, 0.91 mmol) in dry ether (7 mL) was slowly added 1.6 M *n*-BuLi in hexane (0.57 mL, 0.912 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 15 min, 1-[5-methoxy-2-(4-methoxyphenyl)-4-thiazolyl]perfluorocyclopentene[6] (160 mg, 0.387 mmol) in dry ether (2 mL) was added at −100 °C. The reaction mixture was further stirred at −80 °C for 3 h, and then distilled water was added. The product was extracted with ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 2/8) and HPLC (ethyl acetate/hexane = 2.5/7.5) to afford to 180 mg (36%) of **3a** as solid: mp 103–104 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.01 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 1.76 (s, 3H), 1.62 (s, 3H); MS m/z 555 [M^+]. Calcd for $C_{27}H_{23}F_6NO_3S$: C, 58.37; H, 4.17; N, 2.52%. Found: C, 58.63; H, 4.32; N, 2.52%.

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Supporting Information

^{1}H NMR chart (Figure S1). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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