

Synthesis of Novel Thermally Reversible Photochromic Spiro[adamantane-2,7'(6'H)-benzothiophene]

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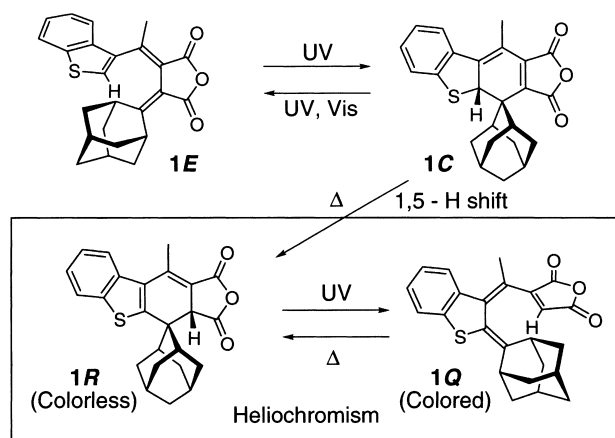
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A new thermally reversible photochromic compound, 4',5'-hexafluoropropano-6'-phenylspiro[adamantane-2,7'(6'H)-benzothiophene], derived from UV-irradiation of 2-(1-adamantyldiene-1-phenylmethyl)-3,3,4,4,5,5-hexafluoro-1-(3-thienyl)cyclopentene via the photochemical 6π -electrocyclization followed by the thermal 1,5-hydrogen migration, was synthesized and its photochemical and thermal properties were examined. The structurally more simplified 3,3,4,4,5,5-hexafluoro-2-(2-methyl-1-phenyl-1-propenyl)-1-(3-thienyl)cyclopentene did not yield the thermally reversible photochromic compound upon UV irradiation.

In order to realize a molecular or supramolecular system whose physical as well as chemical properties can be switched from outside of the system, photochromic molecules are suitable because all of their properties, including the structure and absorption spectral properties, can be changed by light irradiation. Although there have been found and developed so many photochromic compounds, the submission of a new class of compounds to increase the assortment in the showcase of photochromic compounds is still important because of adequate selection for a particular use in the future, such as optical recording, opto-electronic switching and the auto-regulation of light.

Photochromic compounds are categorized into two classes. One is that conversion between the stable states occurs only by photoirradiation (P-type); the other is that conversion occurs by photoirradiation as well as a thermal treatment (T-type). A unique category is so-called "heliochromism," which belongs to T-type photochromism. For fulgide¹ derivatives, Whittall stated that "the heliochromic compounds have high efficiency for coloring with near UV irradiation while the colored forms have a low efficiency for photochemical reverse action but have thermal reverse at ambient temperatures so that these compounds color in sunlight".² The structural features of these heliochromic fulgides (heliofulgides)³ like **1** are: (1) they have a hydrogen atom at the terminal olefin of the hexatriene moiety on the aromatic ring, and (2) they have an adamantylidene group as the other terminal of the hexatriene moiety, although the reason is not clear. The mechanism for the heliochromism of **1** is shown in Scheme 1.

As a part of our research to seek new photochromic systems,⁴ we envisioned that arylbutadienes may produce a new photochromic class of compounds based on 6π -electrocyclization. This article deals with a new T-type photochromic com-



Scheme 1. Heliochromism of a benzothiénylfulgide.

pound produced from the arylbutadiene; a following article will deal with new P-type photochromic arylbutadienes.

Results and Discussion

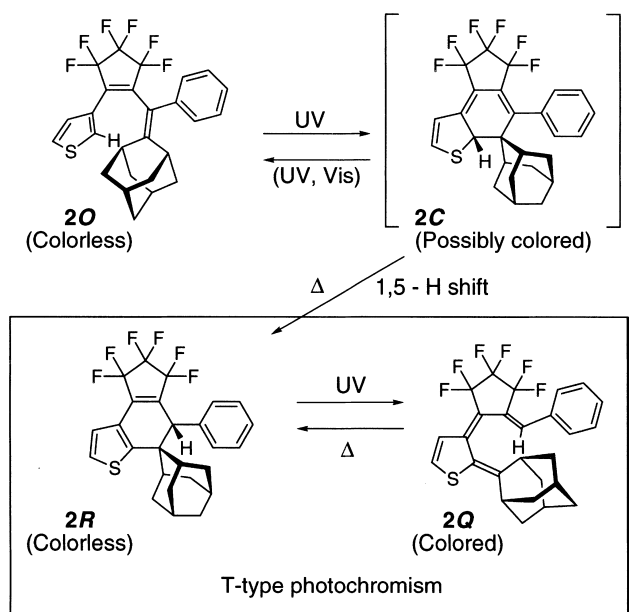
Design of the Molecules. The necessary units for thermally reversible photochromic molecules like **1** are: (i) an aryl group as one of two terminal double bonds which does not have a substituent on the bond-forming carbon atom upon photoirradiation, (ii) an adamantylidene group as the other terminal double bond, and (iii) the central double bond of the hexatriene moiety. To append photochemical fatigue resistivity as well as to remove the energy-wasting *E*-*Z* isomerization of the olefin, we employed perfluorocyclopentene, which is frequently used for diarylethenes,⁵ as the central ethene moiety. The aryl group is attached to the perfluorocyclopentene ring with its C-3, and a hydrogen atom is necessary on C-2. In

order to secure the possibility to tune the absorption maximum of the colored form as the later modification, a phenyl group participating in the conjugation may be useful. Consequently, we chose **2** as the target molecule. The anticipated reaction course of **2** is shown in Scheme 2.

To clarify the generality of the photochromic reaction, we also designed a simpler molecule **3**, which has an isopropylidene group instead of the adamantylidene group.

Synthesis of 2O. The synthesis of **2** was carried out as shown in Scheme 3. The right part **7** was prepared in four steps in 43% yield, starting from 2-adamantanone and benzylmagnesium chloride. After the right part was attached to perfluorocyclopentene in 92% yield to form **8**, 3-lithiothiophene, generated from 3-bromothiophene, was introduced to **8** to accomplish the synthesis of **2O** in 20% yield.

Structure Determination of 2. In order to obtain the T-type photochromic compound, a toluene solution of **2O** was irradiated with 313-nm light at room temperature for 5 h.



Scheme 2. Photochemical and thermal reactions of **2**.

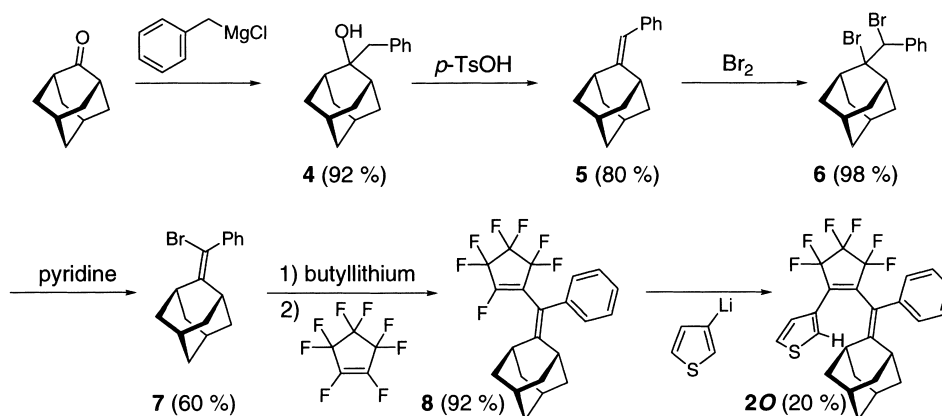
Photochemical 6π -electrocyclization, followed by a thermal sigmatropic 1,5-hydrogen shift, subsequently occurred at r.t. to give **2R** in 57% yield. Because the intermediate **2C** was not detected by UV-vis spectroscopy, the hydrogen rearrangement to give **2R** from **2C** occurred rapidly. The structure of **2R** was determined by ^1H NMR, IR, MS, and finally X-ray crystallographic analysis. The chemical shift of the migrated hydrogen of **2R** appeared at δ 4.57 in CDCl_3 , which is in good agreement with the chemical shift of that of the heliofulgide **9R**⁶ (Chart 1; δ 4.20). The structure of **2R** was unequivocally determined by X-ray crystallographic analysis. An ORTEP drawing is shown in Fig. 1, and the crystallographic data are listed in Table 1. It is thus clarified that the photochemical electrocyclization of **2O** to give **2C** followed by hydrogen migration on **2C** occurred to afford **2R**.

Photocoloration of 2R and Thermal Decoloration of 2Q.

When **2R** in toluene was irradiated with 313-nm light, all of the absorption above 300 nm increased with the emergence of a new absorption band in the visible region (λ_{max} 500 nm). The changes in the absorption spectra by 313-nm light irradiation in toluene at room temperature and by a thermal treatment to cause a back reaction are shown in Fig. 2. Although an observation of ^1H NMR spectra of the colored species was not successful because of its low concentration as well as the internal filter effect of **2R**, the colored species was assigned to the ortho-quinodimethane-type compound **2Q** as an analogy with **1Q**. The absorption of **2Q** became smaller when the solution was kept in the dark at room temperature, and disappeared completely within 150 min. Because the coloration-decoloration cycles were repeatable many times, it was proved that **2R** and **2Q** compose the thermally reversible photochromic system.

The decoloration rate constants at different temperatures in toluene are given in Table 2. The activation energy of decoloration in toluene was calculated to be 84.0 kJ mol^{-1} .

Simplified Compound 3. The adamantylidene unit is considered to be necessary for heliofulgides to show thermally reversible photochromism.² Because **2** showed thermally reversible photochromism, we intended to replace the adamantylidene group with a simple isopropylidene group in order to know whether the adamantylidene group is also necessary for the present photochromic system. If the replacement would be



Scheme 3. Synthetic route of **2**.

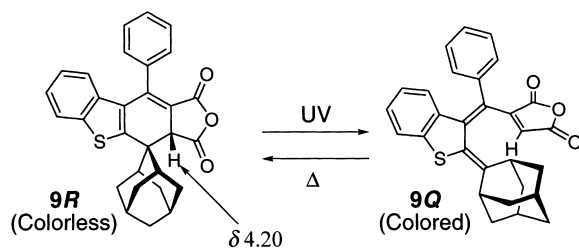
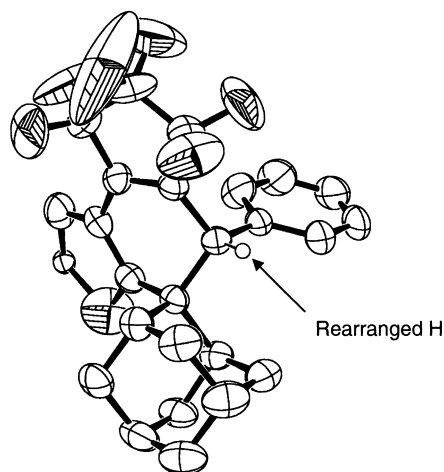


Chart 1. Heliochromic benzothiénylfulgide.

Fig. 1. ORTEP drawing of **2R**.

effective, the molecular design for this system would be more flexible.

The synthesis of **3O** was carried out as shown in Scheme 4 in 13% yield from 2-methyl-1-phenyl-1-propene.

The irradiation of 313-nm light to the toluene solution of **3O** yielded a small amount of the colored species possessing the absorption maximum at 417 nm, together with side products, detected by absorption spectra, HPLC, and ^1H NMR. The ab-

Table 1. Crystallographic Data of **2R**

Empirical Formula	$\text{C}_{26}\text{H}_{22}\text{F}_6\text{S}$
Formula Weight	480.51
Crystal Color, Habit	Colorless, prismatic
Crystal size/mm	$0.5 \times 0.5 \times 0.5$
Crystal System	Monoclinic
Lattice Type	Primitive
$a/\text{\AA}$	11.339(2)
$b/\text{\AA}$	9.760(2)
$c/\text{\AA}$	19.868(2)
β/degree	97.20(1)
Volume/ $\text{\AA}^3$	2181.4(6)
Space Group	$P2_1/c$ (No. 14)
Z	4
Density (calculated)/ g cm^{-3}	1.463
Residuals: R ; R_w (all data)	0.203; 0.469
Residuals: $R1$ (for $I > 2.0\sigma(I)$)	0.141
Goodness-of-fit Indicator	2.21

sorption band in the visible region did not fade when the solution was kept in the dark at room temperature for a few hours. Instead, the color disappeared upon visible-light irradiation, and the increase in the amount of **3O** was then detected by HPLC.

The photoreaction was followed by ^1H NMR in toluene- d_8 . After the irradiation of 313-nm light for about 100 min, two doublet peaks (δ 6.15 and δ 6.35, both d, $J = \text{ca. } 6 \text{ Hz}$) with the same intensity and one doublet (δ 6.24, d, $J = 1.7 \text{ Hz}$) appeared, while most of the signals of the starting material remained. Upon 437-nm light irradiation to the resulting solution for 70 min, the former set of doublet peaks disappeared, while the latter doublet remained unchanged. When 313-nm light was irradiated to the resulting solution for 380 min, the former set of doublet peaks appeared again, and the latter doublet became larger. The former doublets are attributed to the *cis*-oriented olefinic protons on the dihydrothiophene ring, that

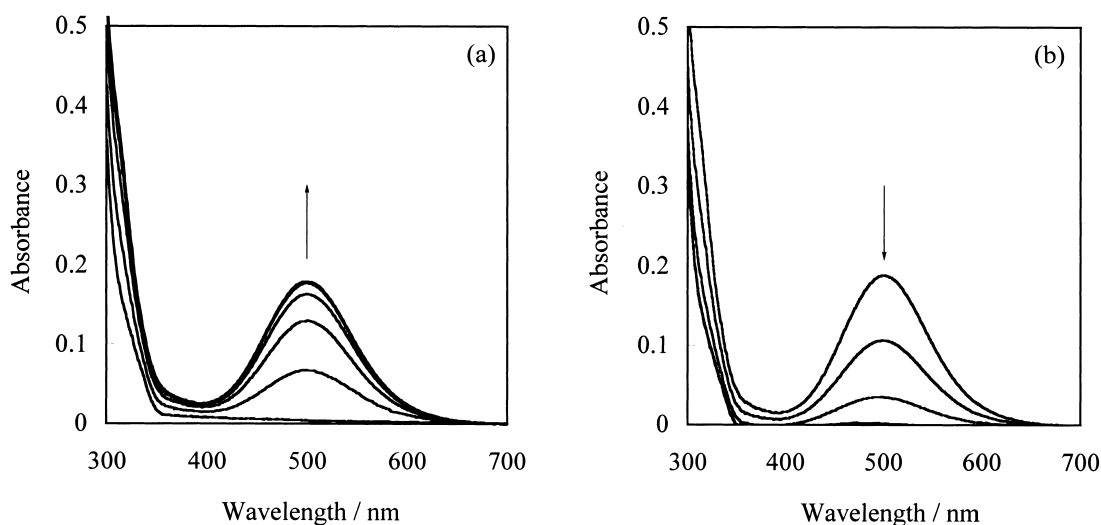


Fig. 2. Change in absorption spectra of **2** in toluene. (a) During 313-nm light irradiation to **2R**. Irradiation time/min; 0, 1, 3, 5, 7, 8. (b) When the solution of **2R** irradiated with 313-nm light for 8 min was kept at 26.2 °C in the dark. Time/min; 0, 20, 60, 150.

Table 2. Decoloration Rate Constants k at Different Temperatures, Activation Energy E_a , and Preexponential Factor A , of the Reaction from **2Q** to **2R** in Toluene

T/K	k/min^{-1}	$E_a/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$
290.05	7.99×10^{-3}		
299.35	2.84×10^{-2}	84.0	30.1
309.75	7.37×10^{-2}		

can be found in **3C** for example, and the latter one is the proton of an unidentified non-photochromic compound that is produced irreversibly by 313-nm light irradiation on this system.

From the behavior of **3** on HPLC and ^1H NMR during photoirradiation, we concluded that the colored species produced with a small amount should be **3C**, generated by the photochemical 6π -electrocyclization of **3O**. Although prolonged irradiation of 313-nm light caused a decomposition of the compound, no sign of the production of hydrogen-rearranged compound **3R** was observed. Thus, the isopropylidene group is not adequate for this system, and the adamantylidene group is necessary as a terminal substituent to obtain a thermally reversible photochromic compound at this stage. It is clear that the migration of hydrogen is easier for **2C** than **3C**.

In order to explain this result, AM1 semiempirical MO calculations were carried out for **2C** and **3C**. The difference in the atom distances and the bond angle (Scheme 5) may reflect the easiness and difficulty for the migration of the hydrogen on C_α (H_m). The data are given in Table 3. Both bond lengths of $\text{C}_\alpha\text{--C}_\beta$ and $\text{C}_\beta\text{--C}_\gamma$ in **2C** are longer than those in **3C**. As a result, the angle $\text{C}_\alpha\text{--C}_\beta\text{--C}_\gamma$ in **2C** is smaller than that in **3C**. Therefore, the open space above the cyclohexadiene ring where the hydrogen atom travels along should be larger for **2C** than **3C**. In addition, because the atom distance $\text{H}_m\text{--C}_\gamma$ in **2C** is considerably smaller than that in **3C**, and also the bond length of $\text{C}_\alpha\text{--H}_m$ in **2C** is slightly longer than **3C**, the relevant hydrogen H_m on **2C** can migrate more easily than that on **3C**. Furthermore, although the hydrogen atoms on the methyl group of the isopropylidene moiety on **3C** may disturb the transfer of the hydrogen on C_α by free rotation of the $\text{C}_\beta\text{--C}_\delta\text{H}_3$ bond, whose bond length is shorter than the corresponding bond ($\text{C}_\beta\text{--C}_\delta\text{H}$) in **2C**, the corresponding hydrogen atom on the adamantylidene group in **2C** does not interfere very much, because of the rigidity of the adamantylidene framework.

Similar structural characteristics for the adamantylidene and isopropylidene groups were previously reported for thermally irreversible furylfulgides.⁷ Because the cyclohexadiene ring attaching the adamantylidene group as the spiro-connection is considerably distorted, the steric hindrance over the cyclohexadiene ring became rather small.

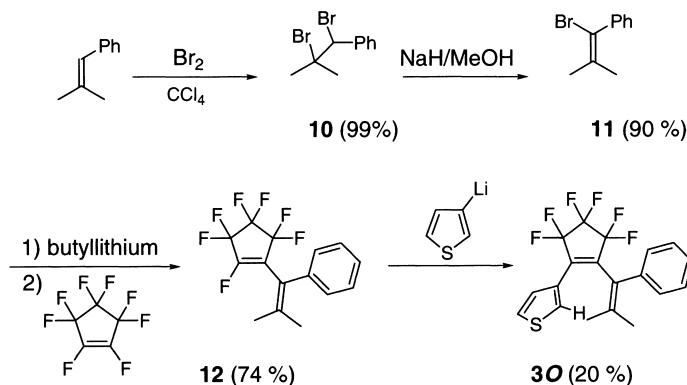
Thus, while the thermal hydrogen migration in **2C** occurred smoothly to yield **2R**, it hardly occurred in **3C**, and the photoirradiation (and less possibly by the application of heat) on **3C** may have caused the side reaction(s). A possible reaction scheme is shown in Scheme 6.

Conclusion

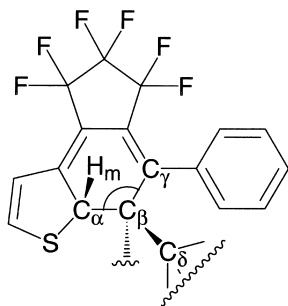
A new thermally reversible photochromic 6,7-dihydrobenzothioiophene **2R** was synthesized. It was prepared from a butadiene **2O**, equipped with a thienyl group, a perfluorocyclopentene ring, a phenyl group, and an adamantylidene group, by way of photochemical 6π -electrocyclization followed by a thermal 1,5-sigmatropic rearrangement. The replacement of the adamantylidene group with the isopropylidene group afforded **3O**, which did not yield the hydrogen-migrated thermally reversible photochromic **3R** by UV irradiation by way of **3C**. The difference in the photochemical and thermal behaviors of **2** and **3** was explained in terms of the steric effect.

Experimental

General. ^1H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) spectrometer in CDCl_3 . The signals are expressed as parts per million down field from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were measured using a Perkin-Elmer 1650 FT-IR spectrometer. Low- and high-resolution mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. UV-vis spectra were recorded on a JASCO Ubest-50 UV-vis spectrophotometer or a JASCO V-550 UV-vis spectrophotometer. The emission line of 313 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (5-cm water filter, a UV-D35 glass filter, 5 cm aqueous $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ solution, 1 cm aqueous $\text{K}_2\text{CrO}_4\text{--NaOH}$ solution, and 1 cm aqueous potassium hydrogen phthalate solution). The emission line of 437 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (5-cm water filter, a Pyrex glass filter, Toshiba glass filters V-40 (two pieces) and Y-43). The silica-gel column chromatographic separation was carried out



Scheme 4. Synthetic route of **3**.



Scheme 5. Bond lengths and angle which showed difference between **2C** and **3C**.

Table 3. Selected Bond lengths and Angles of **2C** and **3C** Obtained by AM1 Calculations

	2C	3C
C _α –C _β bond length/nm	0.1544	0.1528
C _β –C _γ bond length/nm	0.1542	0.1523
C _β –C _δ bond length/nm	0.1543	0.1525
C _α –H _m bond length/nm	0.1131	0.1128
H _m –C _γ atm distance/nm	0.2548	0.2809
C _α –C _β –C _γ angle/°	102.6	109.0

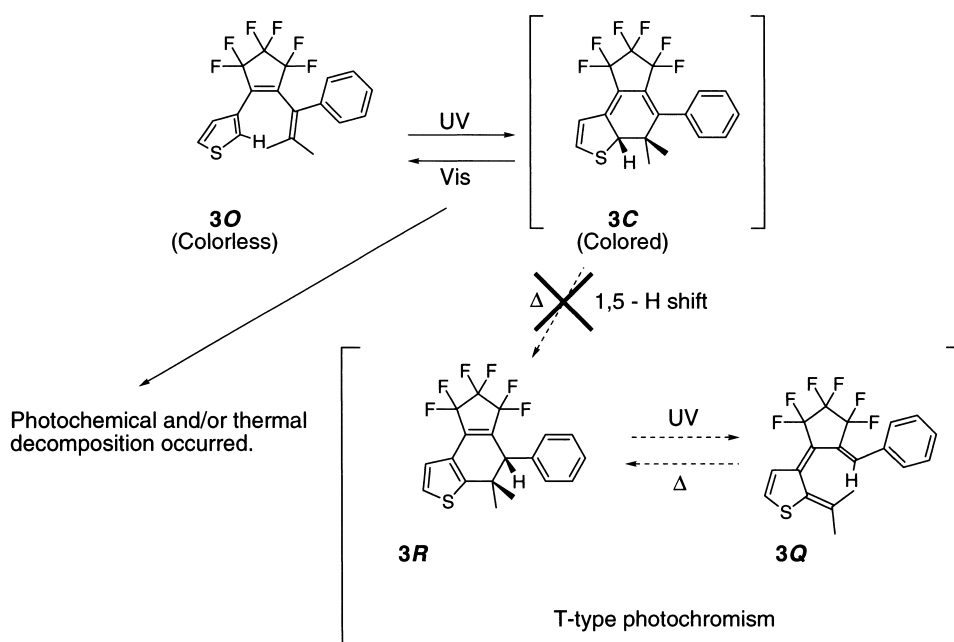
with a Merck Kieselgel 60 (230–400 mesh) with a mixture of ethyl acetate and hexane as an eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25-mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and diethyl ether and dichloromethane were distilled from CaH₂ immediately before use.

Synthesis of 2-Benzyl-2-adamantanol (4). To a solution of 2-adamantanone (4.50 g, 30.0 mmol) in 20 mL THF at 0 °C was

added a 1 mol dm⁻³ THF solution of benzylmagnesium chloride (36 mL, 36 mmol), and the mixture was refluxed for 5 h. The reaction mixture was poured onto an aqueous saturated ammonium chloride solution at 0 °C. The resulting mixture was extracted with ethyl acetate three times, and the combined organic layer was washed with aqueous 10% sodium hydrogencarbonate and saturated brine; the resulting solution was dried with anhydrous sodium sulfate. After the drying agent was filtrated off, the solvent was removed in vacuo, and the residue was purified by silica-gel column chromatography to give **4** (6.72 g, 92%). Mp 59–61 °C. IR (Nujol) ν /cm⁻¹ 3502, 3027, 2919, 702. ¹H NMR (270 MHz, CDCl₃) δ 1.38 (1H, s), 1.49–2.18 (14H, m), 2.99 (2H, s), 7.22–7.34 (5H, m).

Synthesis of 2-Benzylideneadamantane (5). A mixture of 2-benzyl-2-adamantanol **4** (253 mg, 1.04 mmol) and a catalytic amount of 4-toluenesulfonic acid in 20 mL benzene was refluxed for 45 min. To this mixture at r.t. was added aqueous 10% sodium carbonate, and was extracted with ethyl acetate three times. The combined organic layer was washed with aqueous saturated brine, and dried with anhydrous sodium sulfate. The drying agent was removed, and the solvent evaporated. The residue was purified by silica-gel column chromatography to give **5** (187 mg, 80%). Mp 30–32 °C. IR (KBr) ν /cm⁻¹ 3019, 2906, 1446, 696. ¹H NMR (270 MHz, CDCl₃) δ 1.84–1.98 (12H, m), 2.48 (1H, s), 3.15 (1H, s), 6.18 (1H, s), 7.14–7.30 (5H, m).

Synthesis of 2-Bromo-2-(α -bromobenzyl)adamantane (6). To a stirred solution of **5** (517 mg, 2.31 mmol) in 20 mL carbon tetrachloride was added bromine (0.1 mL, 2.3 mmol) at 0 °C, and stirring was continued for 4 h at 0 °C. To the reaction mixture was successively added 20% aqueous sodium thiosulfate and aqueous saturated sodium hydrogencarbonate. The mixture was extracted with ethyl acetate three times, and the combined organic layer was washed with saturated brine. After the organic layer was dried with anhydrous sodium sulfate, the drying agent was removed and the solvent evaporated in vacuo. The residue was purified by silica-gel column chromatography to give **6** (2.21 g, 98%). Mp 102–



Scheme 6. Expected and real photochemical and thermal reactions of **3**.

104 °C. IR (KBr) ν/cm^{-1} 3028, 2903, 1447, 713, 656. ^1H NMR (270 MHz, CDCl_3) δ 1.65–2.71 (14H, m), 5.91 (1H, s), 7.28–7.78 (5H, m).

Synthesis of 2-(α -Bromobenzylidene)adamantane (7). A solution of **6** (4.94 g, 12.2 mmol) in pyridine (15 mL) was stirred at 60 °C for 12 h. After the solvent was removed in vacuo, ethyl acetate was added to the residue, and the organic layer was washed with dil. hydrochloric acid, aqueous 10% sodium hydrogencarbonate, and saturated brine successively, and dried with anhydrous sodium sulfate. The drying agent was removed, and the solvent removed in vacuo. The residue was purified by silica-gel column chromatography to give **7** (2.35 g, 60%). Mp 74–76 °C. IR (KBr) ν/cm^{-1} 3022, 2923, 1446, 735, 693. ^1H NMR (270 MHz, CDCl_3) δ 1.73–1.96 (12H, m), 2.70 (1H, s), 3.30 (1H, s), 7.25–7.35 (5H, m).

Synthesis of 1-(1-Adamantylidene-1-phenylmethyl)-2,3,4,4,5,5-heptafluorocyclopentene (8). To a solution of **7** (465 mg, 1.54 mmol) in 30 mL of THF at –78 °C was added a hexane solution of butyllithium (1.50 mol dm^{-3} , 1.2 mL, 1.84 mmol); the solution was stirred for 30 min. To it was added at that temperature octafluorocyclopentene (0.6 mL, 4.60 mmol), and the resulting mixture was stirred for 15 h. To it was added water, and the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. After the drying agent was removed, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **8** (513 mg, 92%). Mp 85–87 °C. IR (KBr) ν/cm^{-1} 3022, 2923, 1446, 1381, 698. ^1H NMR (270 MHz, CDCl_3) δ 1.57–2.00 (12H, m), 2.50 (1H, s), 2.73 (1H, s), 7.13–7.35 (5H, m). MS (EI, 70 eV) m/z 416 (M^+ , 100), 392 (16), 380 (28), 343 (21), 331 (33). Found: m/z 416.1352. Calcd for $\text{C}_{22}\text{H}_{19}\text{F}_7$: M, 416.1375.

Synthesis of 1-(1-Adamantylidene-1-phenylmethyl)-3,3,4,4,5,5-hexafluoro-2-(3-thienyl)cyclopentene (2O). To a solution of 3-bromothiophene (230 mg, 1.40 mmol) in 30 mL THF at –78 °C was added a hexane solution of butyllithium (1.59 mol dm^{-3} , 0.86 mL, 1.37 mmol). This mixture was added dropwise to a THF (10 mL) solution of **8** (568 mg, 1.37 mmol) at –78 °C, and the resulting mixture was kept stirring for 18 h. After the reaction was quenched with water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. After the drying agent was removed, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **2O** (134 mg, 20%). Mp 103–105 °C. IR (KBr) ν/cm^{-1} 3027, 2917, 1340, 1274, 699. ^1H NMR (270 MHz, CDCl_3) δ 1.25–2.20 (12H, m), 2.51 (1H, s), 3.06 (1H, s), 7.24–7.40 (6H, m), 7.69 (1H, d, J = 5.28 Hz), 8.00 (1H, s). MS (EI, 70 eV) m/z 480 (M^+ , 31), 479 ($(\text{M} - 1)^+$, 100). Found: m/z 480.1292. Calcd for $\text{C}_{26}\text{H}_{22}\text{F}_6\text{S}$: M, 480.1346.

Synthesis of 4',5'-Hexafluoropropano-6'-phenylspiro[adamantane-2,7'(6'H)-benzo[b]thiophene] (2R). A toluene solution of **2O** (ca. 8 mg in 80 mL) was irradiated with 313-nm light for 5 h. The resulting mixture was kept in the dark for 12 h, and the solvent removed in vacuo. This procedure was repeated eight times, and the combined residue was purified by silica-gel column chromatography to give **2R** (36 mg, 57%). Mp 184–185 °C. IR (KBr) ν/cm^{-1} 3027, 2912, 1453, 1259, 700. ^1H NMR (270 MHz, CDCl_3) δ 1.25–2.84 (14H, m), 4.57 (1H, d, J = 8.91 Hz), 6.71 (1H, d, J = 7.59 Hz), 6.79 (1H, d, J = 7.59 Hz), 7.10–7.27 (3H, m), 7.39–7.42 (1H, br), 7.69 (1H, s). MS (EI, 70 eV) m/z 480 (M^+ ,

31), 479 ($(\text{M} - 1)^+$, 100), 388 (22), 347 (8), 333 (20). Found: m/z 480.1385. Calcd for $\text{C}_{26}\text{H}_{22}\text{F}_6\text{S}$: M, 480.1346.

X-ray Crystallographic Analysis of 2R. A colorless prismatic crystal of $\text{C}_{26}\text{H}_{22}\text{F}_6\text{S}$ having approximate dimensions of $0.50 \times 0.50 \times 0.50$ mm, obtained by recrystallization from hexane, was mounted on a glass fiber. All measurements were made on a Rigaku AFC-7R diffractometer with graphite monochromated Mo-K α radiation (λ = 0.71069 Å) and a rotating anode generator. The data were collected at a temperature of 23 ± 1 °C using the ω - 2θ scan technique to a maximum 2θ value of 60.0°. The structure was solved by direct methods⁷ and expanded using Fourier techniques.⁸ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. Several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R and R_w values of 0.203 and 0.469, respectively (6341 all reflections). That the R values and the equivalent thermal factor of some of the fluorine atoms are relatively large may be ascribable to the crystal nature to some extent. The large thermal ellipsoids of some of the fluorine atoms (F(3) and F(4)) may be due to the flip-flop motion of the top CF_2 group of the perfluorocyclopentene ring. However, the structure of the molecule can be discussed unequivocally.

All calculations were performed using the TEXSAN⁹ crystallographic software package of Molecular Structure Corporation. Crystallographic data are summarized in Table 1.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 195759.

Synthesis of 1,2-Dibromo-2-methyl-1-phenylpropane (10). To a stirred solution of 2-methyl-1-phenyl-1-propene (5.03 g, 38.0 mmol) in 80 mL carbon tetrachloride was added bromine (2.33 mL, 7.26 g, 45.4 mmol) at 0 °C, and stirring was continued for 4 h at 0 °C. To the reaction mixture was added 10% aqueous sodium thiosulfate and aqueous saturated sodium hydrogencarbonate successively. The mixture was extracted with dichloromethane three times, and the combined organic layer was washed with saturated brine. After the organic layer was dried with anhydrous sodium sulfate, the drying agent was removed and the solvent evaporated in vacuo. The residue was purified by silica-gel column chromatography to give **10** (10.9 g, 99%) as a yellow liquid. IR (neat) ν/cm^{-1} 3087, 3062, 3030, 2974, 2930, 2864, 1495, 1451, 1386, 1369, 1200, 1098, 743, 699, 614, 567. ^1H NMR (270 MHz, CDCl_3) δ 1.91 (3H, s), 2.01 (3H, s), 5.26 (1H, s), 7.25–7.4 (3H, m), 7.45–7.55 (2H, m). MS (EI, 70 eV) m/z (rel intensity) 293 ($(\text{M} + 4 - \text{H})^+$, 48), 291 ($(\text{M} + 2 - \text{H})^+$, 100), 289 ($(\text{M} - \text{H})^+$, 52).

Synthesis of 1-Bromo-2-methyl-1-phenyl-1-propene (11). To a solution of **10** (10.01 g, 34.27 mmol) in methanol (50 mL) was added a suspension of sodium hydride (60% in mineral oil, 1.54 g, 38.5 mmol, 1.12 equiv) in 60 mL methanol via cannular at r.t., and the resulting mixture was stirred overnight. After adding water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. The drying agent was removed, and the solvent removed in vacuo. The residue was purified by silica-gel column chromatography to give **11** (6.52 g, 90%) as a colorless liquid. IR (neat) ν/cm^{-1} 3055, 2992, 2913, 1487, 1441, 1066, 877, 850, 754, 696, 647. ^1H NMR (270 MHz, CDCl_3) δ 1.72, 2.04 (each 3H, s), 7.2–7.4 (5H, m). MS (EI, 70 eV) m/z 212 ($(\text{M} + 2)^+$, 37), 210 (M^+ , 30), 131 ($(\text{M} - \text{Br})^+$, 100).

Synthesis of 2,3,3,4,4,5,5-Heptafluoro-1-(2-methyl-1-phenyl-1-propenyl)cyclopentene (12). To a solution of **11** (1.99 g, 9.47 mmol) in 80 mL THF at -78°C was added a hexane solution of butyllithium (1.56 mol dm^{-3} , 7.28 mL, 11.36 mmol); the solution was stirred for 30 min. To it was added octafluorocyclopentene (3.8 mL, 6.0 g, 28.41 mmol) at that temperature, and the resulting mixture was stirred overnight. To it was added water, and the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. After the drying agent was removed, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **12** (2.27 g, 74%) as a colorless liquid. IR (KBr) ν/cm^{-1} 3059, 3024, 2991, 2925, 1697, 1380, 1320, 1280, 1200, 1156, 1132, 989, 975, 744, 699, 565. ^1H NMR (270 MHz, CDCl_3) δ 1.78, 1.85 (each 3H, s), 7.13 (2H, d, $J = 6.27\text{ Hz}$), 7.3–7.5 (3H, m). MS (EI, 70 eV) m/z 324 (M^+ , 100), 309 ($(\text{M} - 15)^+$, 85). Found: m/z 324.0758. Calcd for $\text{C}_{15}\text{H}_{11}\text{F}_7$: M, 324.0749.

Synthesis of 3,3,4,4,5,5-Hexafluoro-1-(2-methyl-1-phenyl-1-propenyl)-2-(3-thienyl)cyclopentene (30). To a solution of 3-bromothiophene (460 mg, 2.85 mmol) in 1 mL THF at -78°C was added a hexane solution of butyllithium (1.55 mol dm^{-3} , 1.8 mL, 2.79 mmol) and the mixture was stirred for 3 h. This mixture was added dropwise to a THF (1 mL) solution of **12** (300 mg, 0.93 mmol) at -78°C , and the resulting mixture was kept stirring for 20 h. After the reaction was quenched with water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. After the drying agent was removed, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **30** (72 mg, 20%) as a colorless liquid. IR (neat) ν/cm^{-1} 2992, 2914, 2859, 1492, 1442, 1374, 1341, 1275, 1257, 1214, 1192, 1128, 1080, 1036, 1020, 975, 700. ^1H NMR (270 MHz, CDCl_3) δ 1.70 (3H, s), 1.89 (3H, s), 7.1–7.2 (2H, m), 7.2–7.35 (3H, m), 7.40 (1H, dd, $J = 2.97, 4.95\text{ Hz}$), 7.54 (1H, d, $J = 4.6\text{ Hz}$), 7.94 (1H, br. s). MS (EI, 70 eV) m/z 388 (M^+ , 49), 387 ($(\text{M} - \text{H})^+$, 98), 373 ($(\text{M} - \text{CH}_3)^+$, 71), 372 ($(\text{M} - \text{H} - \text{CH}_3)^+$, 100). Found: m/z 388.0707. Calcd for $\text{C}_{19}\text{H}_{14}\text{F}_6\text{S}$: M, 388.0720.

Photoreaction of 2 and 3 by 313-nm Light Irradiation. A toluene solution ($1.02 \times 10^{-4}\text{ mol dm}^{-3}$ for **2O** and 1.38×10^{-4}

mol dm^{-3} for **3O**) was irradiated with 313-nm light, and the UV-vis spectra were recorded at designated time intervals.

Thermal Decoloration of 2R. A toluene solution of a mixture of **2R** and **2O** obtained by the 313-nm-light irradiation was kept at the designated temperature in the cell holder of a UV-vis spectrometer equipped with a temperature controller, and the decrease in the absorption in the visible region was monitored. Since only **2O** has absorption in the visible region, the decoloration rate constant was calculated from the decrease in the absorption in the visible region.

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