

Fully diastereospecific photochromic reaction of a thiophenophan-1-ene

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Figure S1 shows ^1H NMR spectra of **4a** and **5a** in CDCl_3 recorded at 300 MHz. Since both spectra are quite similar, one can recognize these compounds are enantiomers. The inner methyl groups of thiophene rings appeared at 1.51 ppm and this higher magnetic field shift indicates these methyl groups are shielded by the opposite thiophene rings. That is, the open forms are the photoactive anti-conformations. The dynamic NMR spectra of **5a** are shown in Figure S2 recorded at 298 K, 333 K, and 373K in $(\text{CDCl}_2)_2$. Since there is no change between these spectra, no flipping occurs, then no diastereomerization takes place.

Figure S3 shows HPLC charts of **4a** and photostationary state at 330 nm of **4** separated with Si60 silica-gel column chromatography recorded by absorption at the isosbestic point. The chart reveals that only one diastereomer formed by photoirradiation and the conversion at PSS_{330} was 71%.

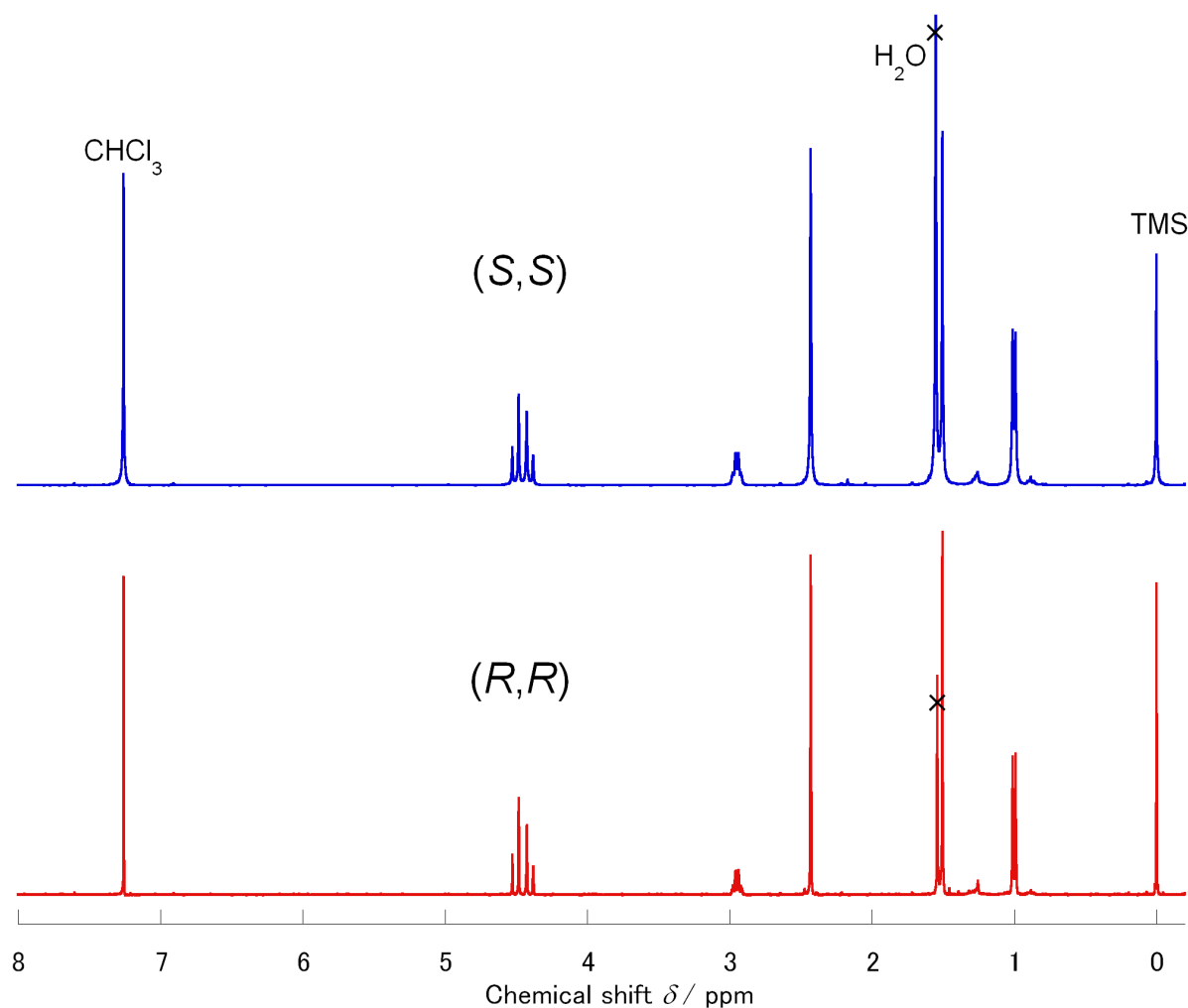


Figure S1 ^1H NMR spectra of **4a** (*R,R*) and **5a** (*S,S*) in CDCl_3 recorded at 300 MHz.

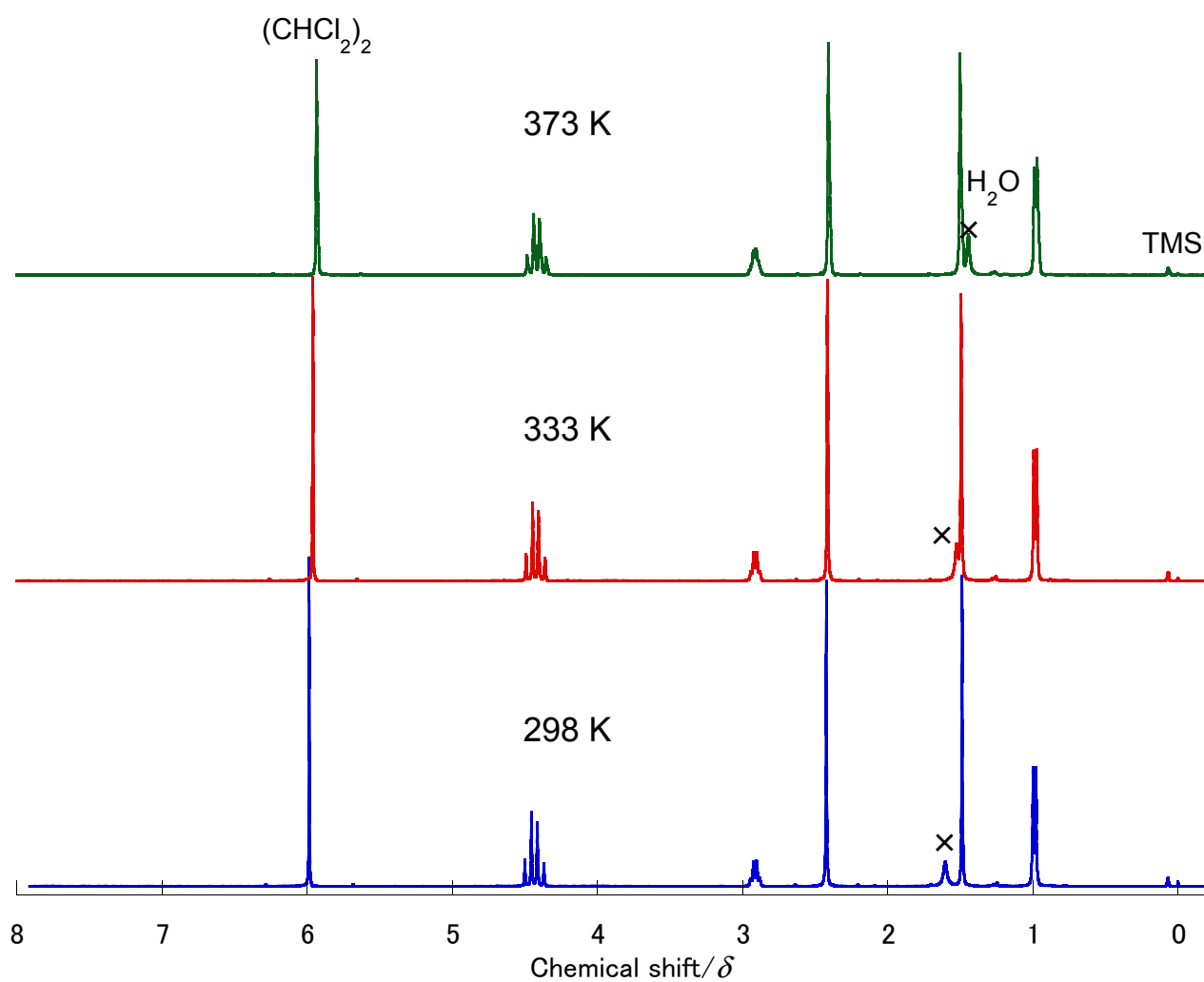


Figure S2 Dynamic ¹H NMR spectra of **5a** (*S,S*) in (CDCl₂)₂ recorded at 300 MHz.

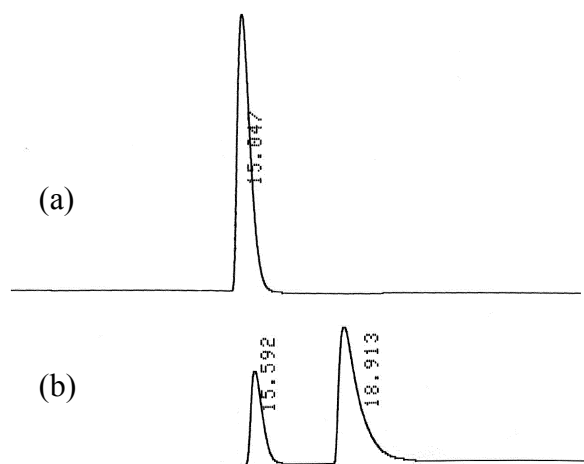


Figure S3 HPLC charts of **4a** (a) and a photostationary state of **4** at 330 nm (b) (Si60, hexane/ethyl acetate (5:1), absorption monitored at isosbestic point).

Figure S4 indicates the most stable conformation of **4a** which is estimated with DFT calculations (B3LYP/4-31G*) in Spartan '08.

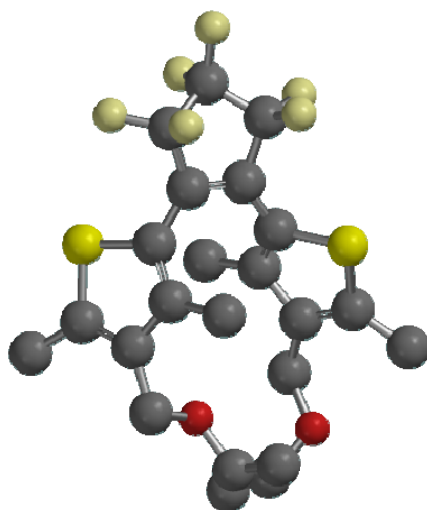


Figure S4 Most stable conformation estimated with DFT calculations (B3LYP/6-31G*).

Figure S5 shows the CD spectra of **5a** (*S,S*) in toluene before and after stored for 2 hours at 100 °C. Since there was no change after heating, diatereomerization did not occur in this condition.

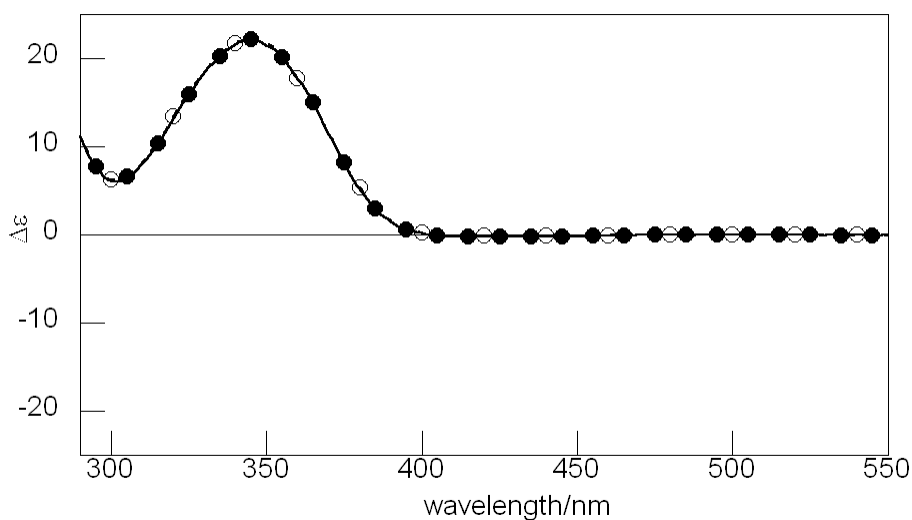


Figure S5 CD spectra of **5a** in toluene before (○) and after (●) stored for 2 hours at 100 °C.

Experimental section

Preparation of (6*R*,7*R*)-6,7-dimethyl-5,8-dioxa-2³,2³,2⁴,2⁴,2⁵,2⁵-hexafluoro-1³,1⁵,3³,3⁵- tetramethyl-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclononaphane (**4a**)

To a refluxing mixture of 331 mg of NaH (13.8 mmol) in 150 ml of dried THF, a solution of 899 mg of **3**¹ (1.33 mmol) and 0.126 ml of (*R,R*)-2,3-butanediol (1.41 mmol) in 90 ml of THF was added

dropwise for 5 hr. The solution was refluxed overnight and brine and AcOEt was added. The organic phase was washed with brine and was dried over MgSO₄. The solvent was evaporated in vacuo and the residue was subjected to a silica-gel column chromatography. Recrystallization of the *n*-hexane/ethyl acetate (10:1) eluate from *n*-hexane afforded 34.6 mg of **4a** (0.068 mmol) in 5.1% yield; yellow prisms (hexane). mp 135-137 °C. δ_{H} (300 MHz; CDCl₃; TMS) 1.00 (6H, d, *J* = 4.5 Hz), 1.51 (6H, s), 2.43 (6H, s), 2.95 (2H, q, *J* = 4.5 Hz), 4.40 (2H, d, *J* = 14 Hz), 4.51 (2H, d, *J* = 13 Hz), HRMS (EI): *m/z* = 510.1136 (M⁺), Calc. for C₂₃H₂₄O₂F₆S₂: 510.1122. [α]_D = +650° (toluene, *c* = 5.2×10⁻³ g dL⁻¹)

Preparation of (6*S*,7*S*)-6,7-dimethyl-5,8-dioxo-2³,2³,2⁴,2⁴,2⁵,2⁵-hexafluoro-1³,1⁵,3³,3⁵- tetramethyl-2(1,2)-cyclopentena-1,3(2,4)dithiophenacyclononaphane (**5a**)

Compound **5a** was prepared in a similar manner to that described for **4a**. Recrystallization of the *n*-hexane/ethyl acetate (10:1) eluate from *n*-hexane afforded 30.7 mg of **5a** (0.060 mmol) in 4.5% yield; yellow prisms (hexane). mp 135-137 °C. δ_{H} (300 MHz; CDCl₃; TMS) 1.00 (6H, d, *J* = 4.5 Hz), 1.51 (6H, s), 2.43 (6H, s), 2.95 (2H, q, *J* = 4.5 Hz), 4.40 (2H, d, *J* = 14 Hz), 4.51 (2H, d, *J* = 13 Hz), HRMS (EI): *m/z* = 510.1122 (M⁺), Calc. for C₂₃H₂₄O₂F₆S₂: 510.1122, [α]_D = -640° (toluene, *c* = 5.2×10⁻³ g dL⁻¹)

Reference

- 1 M. Takeshita, C. Tanaka, T. Miyazaki, Y. Fukushima and M. Nagai, *New J. Chem.*, 2009, **33**, 1433.