

Supplementary Information for

**Photochromic and self-assembling properties of diarylethenes having chiral
amphiphilic side chains at the reactive carbon atoms**

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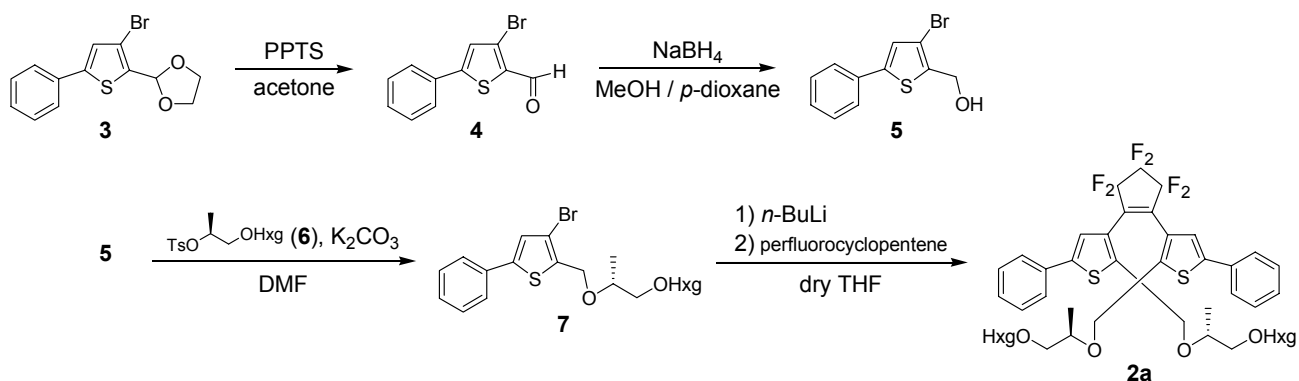
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Experimental Section.

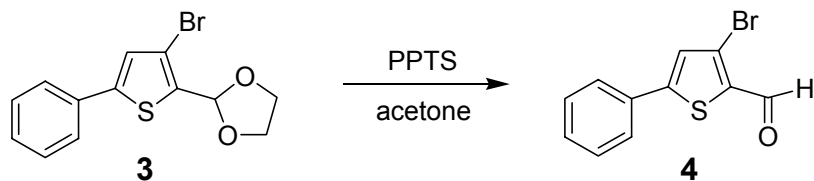
A. Materials.

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 Chemical, 63-210 mesh). $^1\text{H-NMR}$ spectra were recorded on a Bruker AVANCE 400 instrument. Samples were dissolved in CDCl_3 and tetramethylsilane was used as an internal standard. Mass spectra were obtained by a JEOL JMS-HX110A, a JMS-SX102A, and a BRUKER autoflex-KK MALDI TOF mass spectrometer. 2-(3-Bromo-5-phenyl-thiophen-2-yl)-[1,3]dioxolane (**3**)¹ and tosylated derivative of poly(ethylene glycol) monomethyl ether (**6**)² were prepared according to the method reported previously. *p*-toluene sulfonic acid monohydrate and pyridinium-*p*-toluene sulfonate were purchased from TCI.

Scheme S1. Synthesis of compound **2a**.



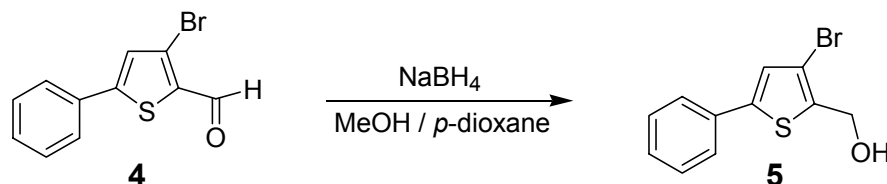
3-Bromo-5-phenyl-thiophene-2-carbaldehyde (4)



To a solution of 2-(3-bromo-5-phenylthiophen-2-yl)-[1,3]dioxolane (**3**)¹ (1.46 g, 4.69 mmol) in acetone (50 mL) was added pyridinium-*p*-toluene sulfonate (PPTS, 2.30 g, 9.15 mmol). The solution was stirred for 4 h at room temperature. The reaction product was extracted with diethyl ether (× 3), and the organic layer was washed with brine (× 2), dried over MgSO₄, filtrated, and evaporated. The crude product was purified by recrystallization to yield **4** (685 mg, 2.56 mmol, 54.6%) as a yellow solid.

¹H-NMR (CDCl₃, TMS, 400 MHz) δ 7.35 (s, 1 H), 7.41-7.52 (m, 3 H), 7.61-7.67 (m, 2 H), 9.95 (s, 1 H); EI HRMS (*m/z*) [M]⁺ calcd for C₁₁H₇BrOS⁺: 265.9395, found: 265.9398.

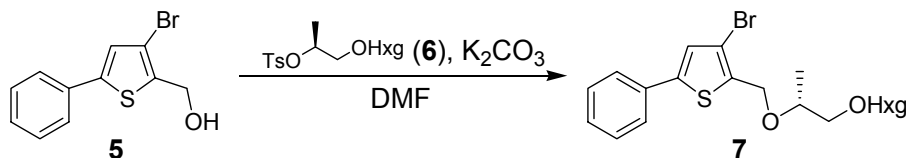
(3-Bromo-5-phenyl-thiophen-2-yl)-methanol (5)



To a solution of 3-bromo-5-phenylthiophene-2-carbaldehyde (**4**) (685 mg, 2.56 mmol) in methanol (15 mL) and *p*-dioxane (15 mL) was added NaBH₄ (1.92 g, 50.8 mmol) at 0 °C. The solution was stirred for 1 h. The reaction product was pored into aqueous dilute sulfuric acid and extracted with diethyl ether (× 3). The organic layer was washed with brine (× 2), dried over MgSO₄, filtrated, and evaporated to yield **5** (660 mg, 2.45 mmol, 95.7%) as a white powder.

¹H-NMR (CDCl₃, TMS, 400 MHz) δ 1.94 (bs, 1 H), 4.81 (s, 2 H), 7.16 (s, 1 H), 7.27-7.44 (m, 3 H), 7.51-7.58 (m, 2 H); EI HRMS (*m/z*) [M]⁺ calcd for C₁₁H₉BrOS⁺: 267.9552, found: 267.9556.

(*R*)-3-Bromo-2-(2-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethoxymethyl)-5-phenyl-thiophene (7)

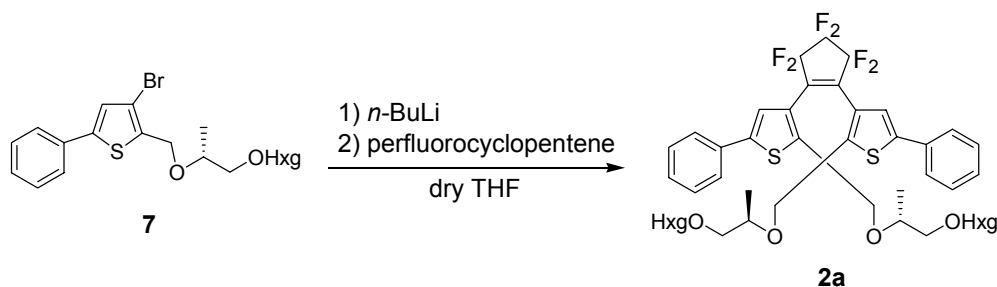


To a solution of NaH (60% in mineral oil, 35.6 mg, 0.89 mmol) in DMF (4 mL), was added (3-bromo-5-phenylthiophen-2-yl)-methanol (**5**) (200 mg, 0.74 mmol) at 0 °C under argon atmosphere. The solution was stirred for about 10 minutes. After the addition of (*S*)-toluene-4-sulfonic acid 2-{2-[2-(2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-1-methyl-ethyl ester (**6**)² (376 mg, 0.74 mmol), the solution was refluxed for 12 h. The reaction was quenched by the addition of water. The reaction product was extracted with ether (×

3), and the organic layer was washed with brine ($\times 2$), dried over MgSO_4 , filtrated, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate) to yield **7** (122 mg, 0.20 mmol, 27.0%) as a yellow oil.

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ 1.22 (d, $J = 6$ Hz, 3 H), 3.38 (s, 3 H), 3.46-3.90 (m, 24 H), 4.32-4.44 (m, 1 H), 4.75 (s, 2 H), 7.13 (s, 1 H), 7.28-7.34 (m, 1 H), 7.35-7.42 (m, 2 H), 7.51-7.57 (m, 2 H); FAB HRMS (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{42}\text{BrO}_8\text{S}^+$: 605.1778, found: 605.1765.

(*R,R*)-1,2-Bis-[2-{2-(2-[2-{2-(2-[2-methoxy-ethoxy]-ethoxy)-ethoxy]-ethoxy)-ethoxy}-ethoxy)-1-methyl-ethoxymethyl]-5-phenyl-thiophene-3-yl]-perfluorocyclopentene (2a**)**



To a solution of compound **7** (90 mg, 0.149 mmol) in dry THF (0.5 mL) was slowly added *n*-butyllithium hexane solution (1.6 M, 0.098 mL, 0.156 mmol) at -78 °C. After the addition of a solution of perfluorocyclopentene (10 μL , 0.074 mmol) in dry THF (1 mL), the reaction mixture was further stirred for 1 h at that temperature. The reaction was quenched by the addition of water. The reaction product was extracted with ether ($\times 3$), and the organic layer was washed with brine ($\times 2$), dried over MgSO_4 , filtrated, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate \sim ethyl acetate:acetone = 1:1) to yield **2** (22 mg, 0.018 mmol, 24.3%) as a blue oil.

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ 1.04 (d, $J = 6$ Hz, 6 H), 3.39 (s, 6 H), 3.35-3.69 (m, 54 H), 4.02-4.15 (m, 4 H), 7.31-7.37 (m, 4 H), 7.38-7.45 (m, 4 H), 7.57-7.63 (m, 4 H); MALDI-TOF MS (m/z) calcd for $\text{C}_{59}\text{H}_{82}\text{F}_6\text{O}_{16}\text{S}_2\text{Na}$, 1247.48 $[\text{M} + \text{Na}]^+$; found 1247.29 $[\text{M} + \text{Na}]^+$; UV-vis (H_2O) λ_{max} 295 nm; (AcOEt) λ_{max} 283 nm.

Coresponding closed-ring isomer: UV-vis (H_2O) λ_{max} 604 nm; (AcOEt) λ_{max} 585 nm.

B. Photochemical Measurement.

Absorption spectra were measured on a spectrophotometer (Hitachi U-3500). CD spectra were recorded on a JASCO J-720S spectrophotometer. Photoirradiation was carried out using a USHIO 500 W super high-pressure mercury lamp or a USHIO 500 W xenon lamp. Mercury lines of 313 nm and 578 nm were isolated by passing the light through a combination of band-pass filter (UV-D33S) or sharp-cut filter (Y-48) and monochromator (Ritsu MC-20L). Each diastereomer was separated by chiral HPLC (DAICEL co., CHIRALPAC AD-H ($0.46\phi \times 25$ cm, 5 μm), hexane:2-propanol:ethanol = 10:65:25, Flow = 0.25 mL/min for compound **2**.

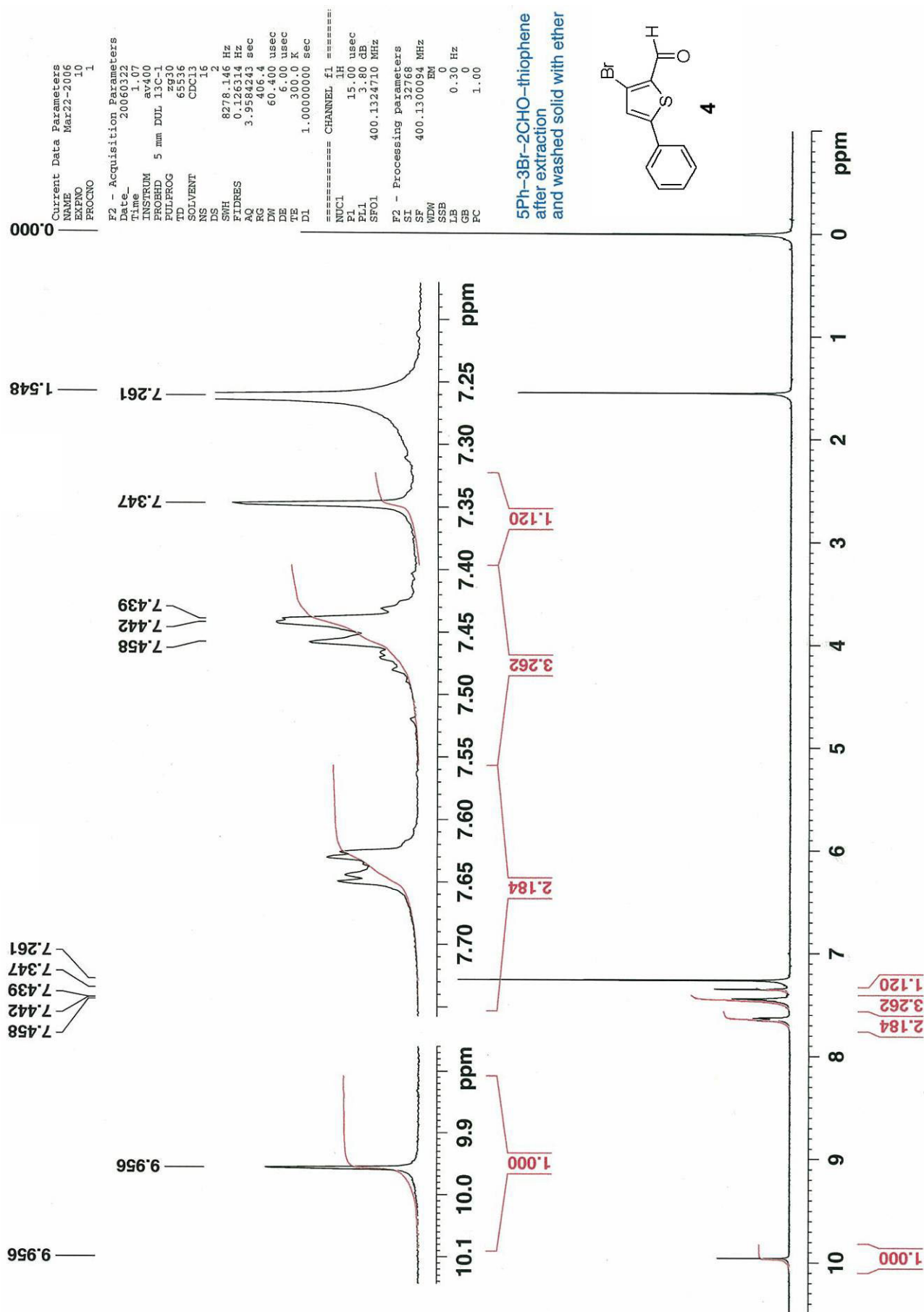


Figure S1. NMR spectrum of 4.

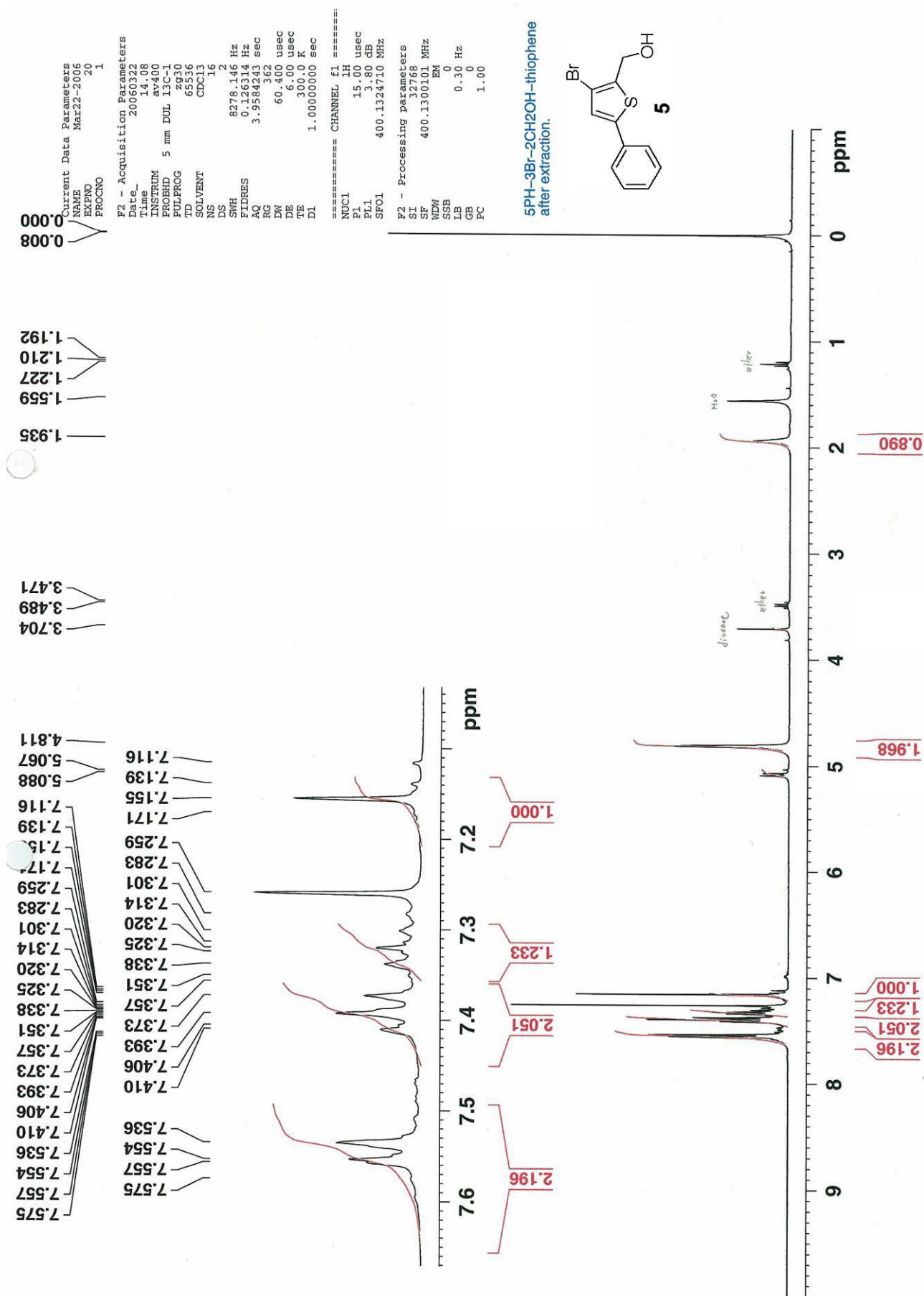


Figure S2. NMR spectrum of 5.

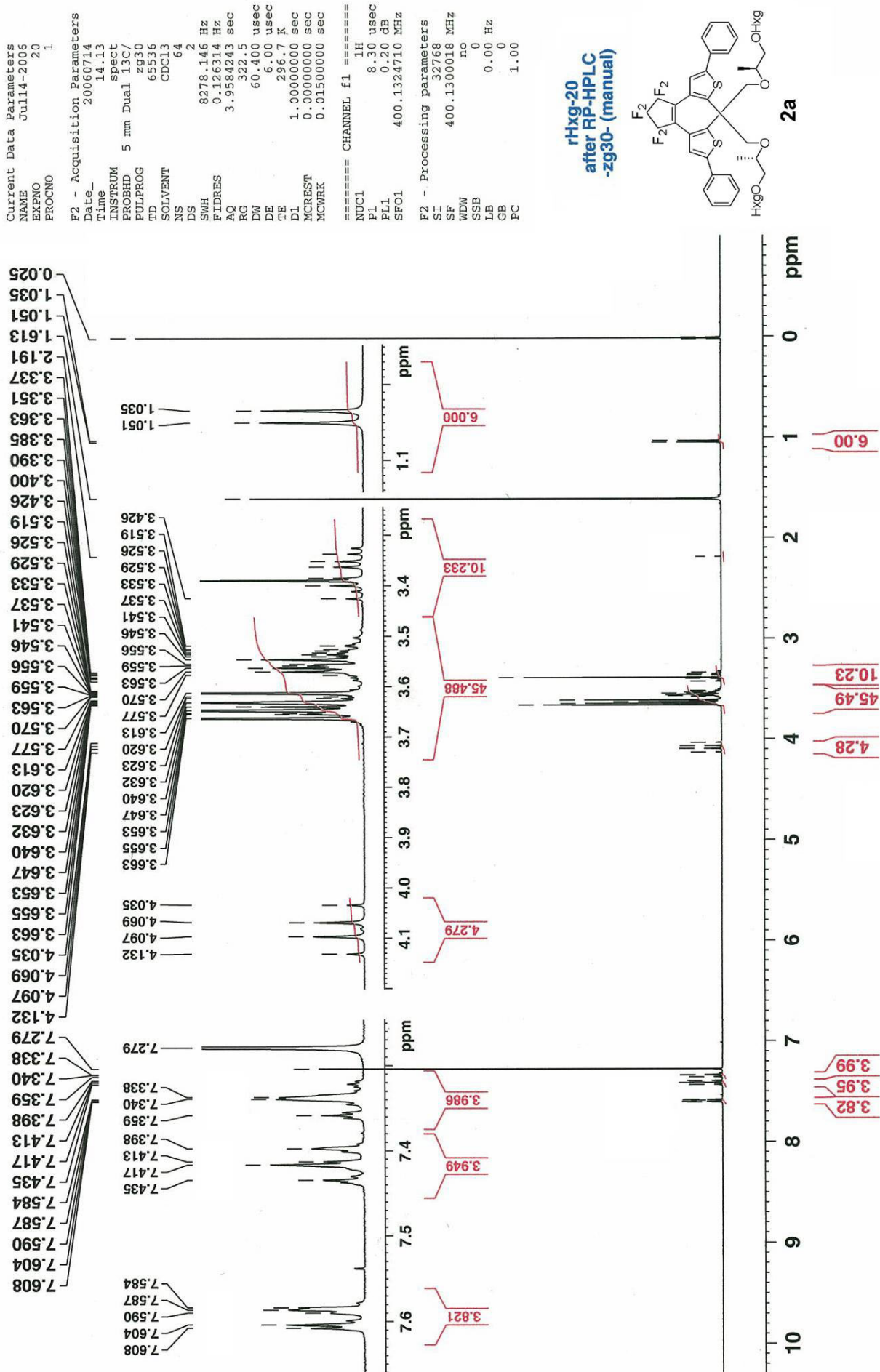
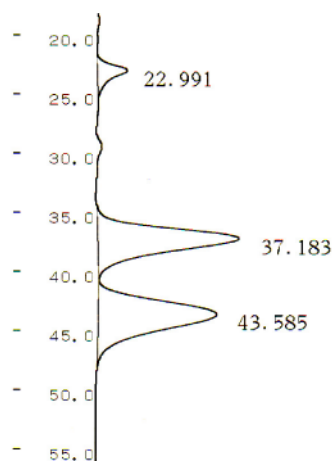
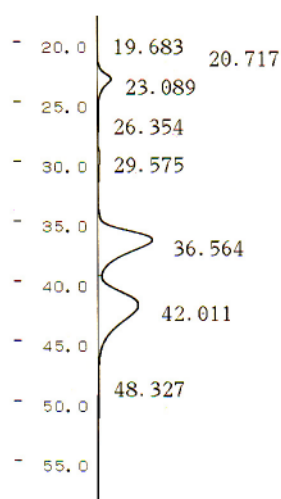


Figure S4. NMR spectrum of **2a**.



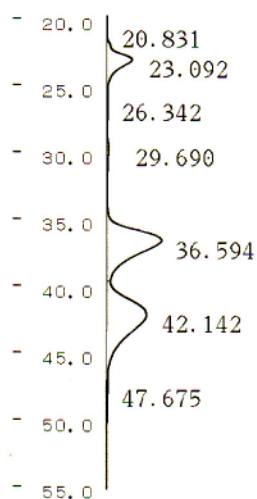
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	4.459	2875	176			0.1796
	2	7.58	10410	260			0.6504
	4	22.991	94675	1171	S		5.9155
	6	37.183	719691	5477			44.9675
	7	43.585	772820	4605			48.287
TOTAL			1600471	11689			100

Figure S5. HPLC chart of **2** measured after irradiation with 313 nm light in ethyl acetate. $d_e = 3.6\%$. The peak with a retention time of ca. 23 min is the open-ring isomer. The peaks with retention times of ca. 37 min and ca. 43 min. are the two closed-ring isomer.



CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	2	8.9	56331	770			0.2685
	3	9.683	19080	662	V		0.0909
	4	10.128	15292	488	V		0.0729
	5	12.196	68058	1284			0.3244
	6	19.683	21659	437			0.1032
	7	20.717	59861	795	V		0.2853
	8	23.089	1484213	16882	V		7.0745
	9	26.354	137133	1186	V		0.6536
	10	29.575	325931	2922	V		1.5536
	11	36.564	9096369	67007			43.358
	12	42.011	9667584	49971	SV		46.0807
	13	48.327	28185	267	T		0.1343
TOTAL			20979696	142670			100

Figure S6. HPLC chart of **2** measured after irradiation with 313 nm light in water at 25 °C (turbid solution). $d_e = 3.0\%$.



CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	11	8.35	61234	762			0.311
	12	10.09	27516	1006	V		0.1397
	13	10.644	34407	1150	V		0.1747
	14	10.92	25153	1066	V		0.1277
	15	11.548	44825	787	V		0.2276
	16	12.772	6117	232	V		0.0311
	17	14.59	8068	149	S		0.041
	19	16.825	21660	390			0.11
	20	17.45	11263	313	V		0.0572
	21	20.831	124658	1172	V		0.633
	22	23.092	2351828	27974	V		11.9429
	23	26.342	163552	1366	V		0.8305
	24	29.69	296790	2495	V		1.5071
	25	36.594	8080050	60074			41.0315
	26	42.142	8408927	43825	SV		42.7015
	27	47.675	26281	290	T		0.1335
TOTAL			19692326	143052			100

Figure S7. HPLC chart of **2** measured after irradiation with 313 nm light in water at 15 °C (clear solution). $d_e = 2.6\%$

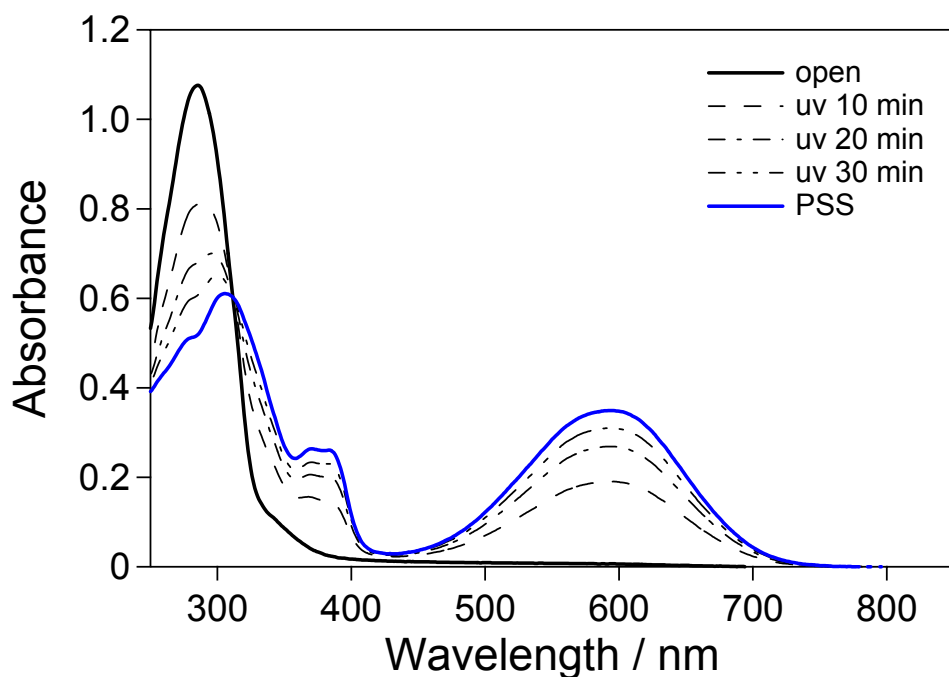


Figure S8. Photochromic spectral change of **2** measured below LCST in water under irradiation with 313 nm light. Irradiation and measurement were performed at 15 °C.

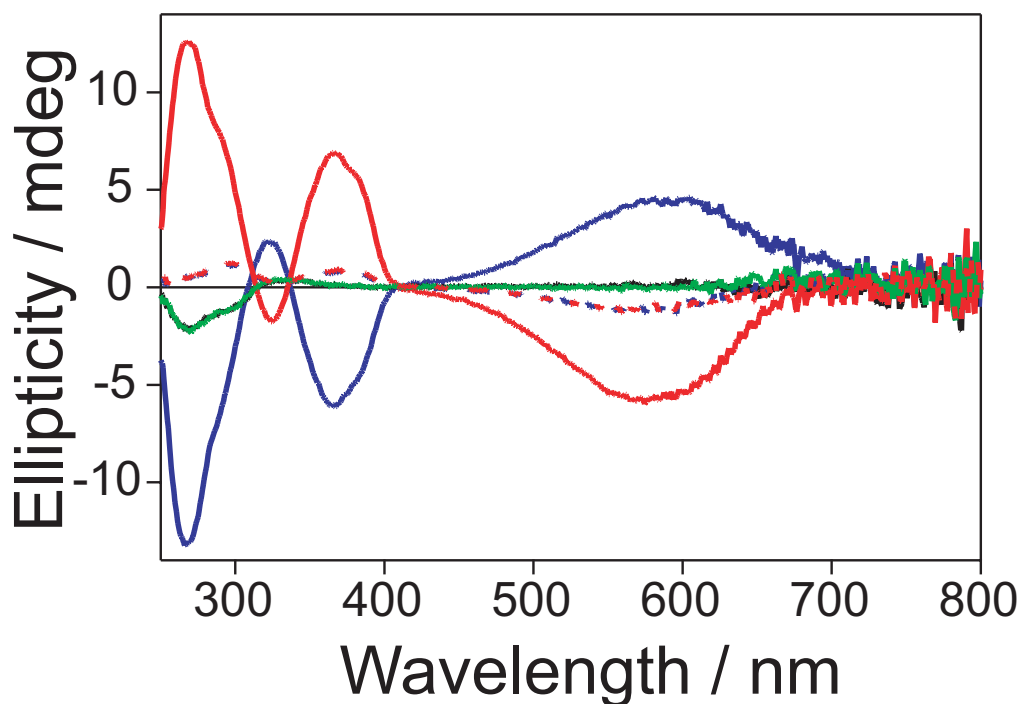


Figure S9. CD spectra of the separated two diastereomers in ethyl acetate. Blue and red solid lines denote the two different isomers. Black and green lines are the corresponding open-ring isomers measured after irradiation with visible light. Blue and red dashed lines are the sample in the photostationary state measured after successive irradiation with 313 nm light.

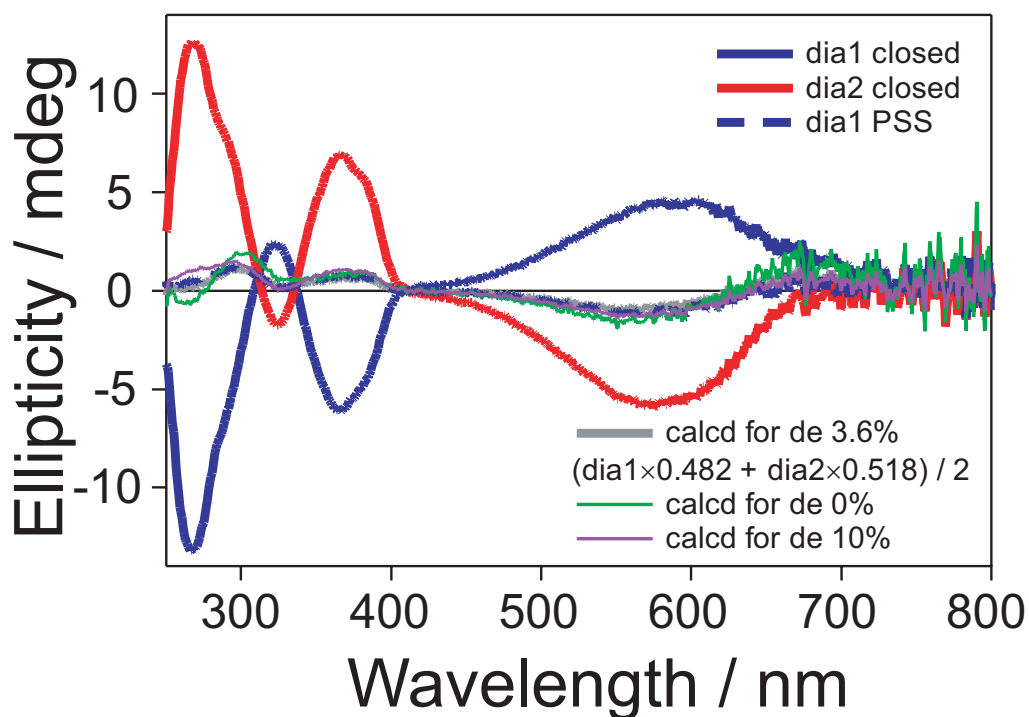


Figure S10. Calculated CD spectra of the closed-ring isomer **2a** with the observed spectra. Red and blue solid line denotes the separated two different diastereomers. Blue dotted lines are the sample in the photostationary state measured after successive irradiation with 313 nm light. Gray line denotes the calculated spectrum with de of 3.6%; green line, 0%; purple line, 10%.

References

1. T. Kodani, K. Matsuda, T. Yamada, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2000, **112**, 9637.
2. T. Hirose, K. Matsuda and M. Irie, *J. Org. Chem.*, 2006, **71**, 7499.