

# Dual-Mode Fluorescence Switching of Photochromic Bisthiazolylcoumarin

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## Electronic Supplementary Information

ESI-1	Experimental details of the synthesis of <b>10</b> , <b>20</b> and <b>30</b>	p. S2
ESI-2	Change in absorption spectra of <b>1</b> , <b>2</b> and <b>3</b> during photoirradiation	p. S7
ESI-3	Photoreaction and fluorescence quantum yields of <b>1</b> , <b>2</b> and <b>3</b>	p. S10
ESI-4	HPLC chromatograms of <b>1</b> , <b>2</b> and <b>3</b> during photoirradiation	p. S12
ESI-5	Change in fluorescence spectra of <b>1</b> and <b>2</b> during photoirradiation	p. S15
ESI-6	Change in absorption spectra of <b>3</b> during acid-base titration	p. S17
ESI-7	Change in fluorescence spectra of <b>3</b> during acid-base titration	p. S18
ESI-8	Determination of fluorescence quantum yield	p. S20
ESI-9	Change in absorption spectra of <b>3</b> during photoirradiation under basic condition	p. S21
ESI-10	Change in fluorescence spectra of <b>3</b> during photoirradiation under basic condition	p. S23
ESI-11	<sup>1</sup> H NMR spectra of prepared compounds	p. S24

## ESI-1. Experimental details of the synthesis of **10**, **20** and **30**

**General.** Chemical reactions were carried out under a dry nitrogen atmosphere. Anhydrous tetrahydrofuran (THF) was purchased and used as received. Dichloromethane and 1,4-dioxane was freshly distilled from calcium hydride before use. All other solvents were also used as received. Flash column chromatography was carried out on 230-400 mesh silica gel using ethyl acetate and hexane as the eluant. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick silica gel TLC plates.

<sup>1</sup>H NMR Spectra were recorded in deuteriochloroform (CDCl<sub>3</sub>) or deuterated dimethylsulfoxide (DMSO-*d*<sub>6</sub>) with a 300 MHz or 500 MHz NMR spectrometer. The J values are expressed in Hz and quoted chemical shifts are in ppm. The splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. Infrared spectra (IR) were recorded on a FT-IR spectrometer. Low- and high-resolution mass spectra were measured by the electron impact ionization or electrospray ionization using a Mass spectrometer (MS). Ultraviolet (UV) and visible (VIS) spectra were recorded on a UV/Vis spectrophotometer. Fluorescence spectra were recorded on a fluorescence spectrophotometer. The melting points (Mp) were measured using a hot stage microscope and these values were uncorrected. Measurements of the pH values were carried out by using a HORIBA pH meter D-24.

Photochemical reactions were all carried out in a 10-mm path length quartz cell. Photoirradiation with 313-nm light was carried out using a 500-W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a UV-31 glass filter, a UV-D33S glass filter, a 5-cm aqueous NiSO<sub>4</sub>·6H<sub>2</sub>O solution, a 1-cm aqueous K<sub>2</sub>CrO<sub>4</sub> solution, and a 1-cm aqueous potassium diphthalate solution). Photoirradiation with 405-nm light was carried out with a 500 W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a L-39 glass filter, a V-40 glass filter, and a KL-40 interference glass filter). Photoirradiation with 436-nm light was carried out with a 500 W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a Y-43 glass filter, a V-44 glass filter). Photoirradiation with 578-nm light was carried out with a 500 W high-pressure mercury lamp, separated by filters (a 5-cm water filter, a O-57 glass filter, and a KL-58 interference glass filter). Photoirradiation with >500-nm light was carried out with a 500 W high-pressure mercury lamp, separated by filters (a 5-cm water filter, two Y-43 glass filters). During the photoreaction, solutions in the cell were stirred continuously.

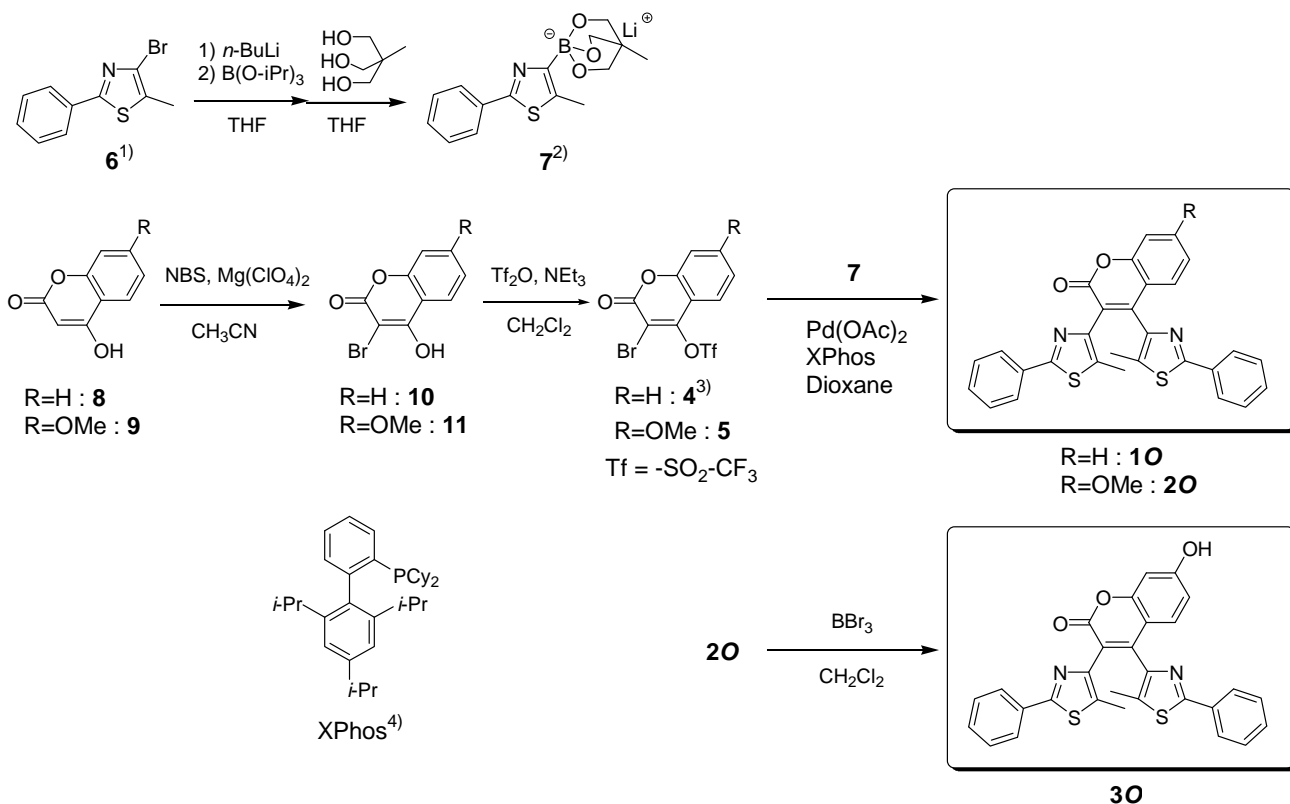
High-performance liquid chromatography (HPLC) equipped with a UV/Vis detector and a silica gel column (Wakosil 5SIL, 4.6-mm diameter x 150-mm length) was used to determine the concentration of isomers during photoirradiation in regard to **1** and **2**. In order to determine the concentration of isomers of **3** during photoirradiation, an HPLC apparatus equipped with reversed-phase column (WakoPak Navi C18-5, 4.6-mm diameter x 250-mm length) was used. HPLC grade acetonitrile and 40 mmol dm<sup>-3</sup> sodium acetate buffer solution were used as eluent.

Quantum yields were determined according to the method described in our previous paper.<sup>1)</sup>

- 1) Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi and Y. Kurita, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3297–3303.

### Synthesis of **10**, **20** and **30**

Synthesis of **10**, **20** and **30** were carried out according to the following procedures.



- 1) K. Uchida, T. Ishikawa, M. Takeshita and M. Irie, *Tetrahedron*, 1998, **54**, 6627–6638.  
2) Y. Yamamoto, M. Takizawa, X. Q. Yu and N. Miyaura, *Angew. Chem., Int. Ed.*, 2008, **47**, 928–931.  
3) L. Zhang, T. Meng, R. Fan and J. Wu, *J. Org. Chem.*, 2007, **72**, 7279–7286.  
4) K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3358–3366.

### Synthesis of (5-methyl-2-phenyl-4-thiazolyl)cyclic-triolborate lithium salt (**7**).

To a solution of 4-bromo-5-methyl-2-phenylthiazole (**6**) (1.22 g, 4.81 mmol, 1.00 eq) in anhydrous THF (34 mL) was added dropwise a hexane solution of *n*-butyllithium (2.63 mol dm<sup>-3</sup>, 2.00 mL, 5.26 mmol, 1.09 eq) at -78 °C under a N<sub>2</sub> atmosphere. The resulting solution was stirred at this temperature for 1 h, then triisopropylborate (1.40 mL, 6.10 mmol, 1.27 eq) was added quickly, and the mixture was stirred for overnight with gradual warming up to room temperature. A solution of 1,1,1-tris(hydroxymethyl)ethane (0.587 g, 4.88 mmol, 1.02 eq) in anhydrous THF (20 mL) was then added through a cannula, and the resulting mixture was stirred for 5h. Concentration to dryness under reduced pressure gave crude 1.74 g of **7** as a brown solid.

Mp >330 °C.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, TMS) δ/ppm 0.54 (3H, s), 2.47 (3H, s), 3.70 (6H, s), 7.43 (3H, m), 7.86 (2H, m). (**Fig. S22**).

IR (neat)  $\nu/\text{cm}^{-1}$  2958, 2869, 2362, 1734, 1456, 1374, 1231, 1069, 979, 930, 761, 688.

LRMS (EI, 70 eV) *m/z* (rel intensity), 303 ((M-Li+1)<sup>+</sup>, 53), 263 ((M-46)<sup>+</sup>, 100), 234 ((M-75)<sup>+</sup>, 54), 207 ((M-102)<sup>+</sup>, 78), 175 ((M-134)<sup>+</sup>, 59).

### Synthesis of 3-bromo-4-hydroxy-7-methoxycoumarin (**11**).

A mixture of 4-hydroxy-7-methoxycoumarin (**9**) (806 mg, 4.19 mmol, 1.00 eq), *N*-bromosuccinimide (828 mg, 4.65 mmol, 1.11 eq) and Mg(ClO<sub>4</sub>)<sub>2</sub> (299 mg, 1.34 mmol, 0.32 eq) in acetonitrile (120 mL) was stirred for 5h at room temperature under a N<sub>2</sub> atmosphere. The reaction mixture was extracted with ethyl ether. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, and the solvent evaporated. The residue was dried and used without further purification and characterization.

### Synthesis of 3-bromo-4-trifluoromethanesulfonyloxy-7-methoxycoumarin (**5**).

To a solution of 3-bromo-4-hydroxy-7-methoxycoumarin (**11**) and triethylamine (1.07 mL, 7.58 mmol, 1.81 eq) in anhydrous dichloromethane (130 mL) was added dropwise trifluoromethanesulfonic anhydride (1.06 mL, 6.30 mmol, 1.50 eq) at 0 °C under a N<sub>2</sub> atmosphere. The resulting solution was stirred at room temperature for 30 min, and then was evaporated under reduced pressure. The residue was purified directly by column chromatography on silica gel using ethyl acetate / hexane (15%) as the eluent, to give 825 mg (2.05 mmol) of **5** as a white solid in 49% yield.

Mp 129-132 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ/ppm 3.93 (3H, s), 6.91 (1H, d, *J*/Hz=2.4), 6.99 (1H, dd, *J*/Hz=8.8, 2.4), 7.64 (1H, d, *J*/Hz=8.8). (**Fig. S23**).

IR (neat)  $\nu/\text{cm}^{-1}$  3078, 3009, 2364, 1737, 1603, 1426, 1357, 1211, 1126, 1053, 1018, 934, 805, 587.

LRMS (EI, 70 eV) *m/z* (rel intensity), 404 ((M+2)<sup>+</sup>, 100), 402 (M<sup>+</sup>, 97), 243 ((M-159)<sup>+</sup>, 75), 241 ((M-161)<sup>+</sup>, 75)

### Synthesis of 3,4-bis(5-methyl-2-phenyl-4-thiazolyl)-coumarin (**10**).

A suspension of (5-methyl-2-phenyl-4-thiazolyl)cyclic-triolborate lithium salt (**7**) (3.29 g, 10.65 mmol, 4.18 eq), 3-bromo-4-trifluoromethanesulfonyloxycoumarin (**4**) (0.950 g, 2.55 mmol, 1.00 eq), palladium acetate (94.8 mg, 0.42 mmol, 0.16 eq) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos) (249 mg, 0.52 mmol, 0.20 eq) in anhydrous 1,4-dioxane (5 mL) was heated for 15 min at 160 °C by microwaves. The reaction mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, and the solvent evaporated. The residue was purified by

column chromatography on silica gel using ethyl acetate / hexane (20 %) as the eluent.

After the solvent evaporated, the residue was reprecipitated with chloroform / hexane to give 144 mg (0.292 mmol) of **1O** as a white solid in 12% yield.

Mp 182-184 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS) δ/ppm 2.17 (3H, s), 2.34 (3H, s), 7.27 (4H, m), 7.42 (5H, m), 7.57 (1H, m), 7.72 (2H, d, J/Hz=4.2), 7.88 (2H, m) (**Fig. S24**).

IR (neat) v/cm<sup>-1</sup> 3062, 2360, 1712, 1601, 1498, 1463, 1272, 1194, 993, 972, 751, 687.

LRMS (EI, 70 eV) m/z (rel intensity), 492 (M<sup>+</sup>, 100), 491 ((M-1)<sup>+</sup>, 76), 477 ((M-CH<sub>3</sub>)<sup>+</sup>, 41).

Found: m/z 492.09986, Calcd for C<sub>29</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: M, 492.09663.

### Synthesis of 3,4-bis(5-methyl-2-phenyl-4-thiazolyl)-7-methoxycoumarin (**2O**).

A suspension of (5-methyl-2-phenyl-4-thiazolyl)cyclic-triolborate lithium salt (**7**) (3.16 g, 10.2 mmol, 4.92 eq), 3-bromo-4-trifluoromethanesulfonyloxy-7-methoxycoumarin (**5**) (0.838 g, 2.08 mmol, 1.00 eq), palladium acetate (32.0 mg, 0.143 mmol, 0.69 eq) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos) (120 mg, 0.252 mmol, 0.12 eq) in anhydrous 1,4-dioxane (8 mL) was heated for 15 min at 160 °C by microwaves. The reaction mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (20 %) as the eluent. After the solvent evaporated, the residue was reprecipitated with chloroform / hexane to give 221 mg (0.423 mmol) of **2O** as a white solid in 20% yield.

Mp 150-153 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ/ppm 2.16 (3H, s), 2.32 (3H, s), 3.91 (3H, s), 6.82 (1H, dd, J/Hz=8.8, 2.4), 6.94 (1H, d, J/Hz=2.4), 7.25-7.35 (4H, m), 7.43 (3H, m), 7.71 (2H, m), 7.88 (2H, m) (**Fig. S25**).

IR (neat) v/cm<sup>-1</sup> 2966, 2367, 2183, 1723, 1607, 1460, 1288, 1145, 1029, 762, 687.

LRMS (EI, 70 eV) m/z (rel intensity), 523 ((M+1)<sup>+</sup>, 39), 522 (M<sup>+</sup>, 100), 521 ((M-1)<sup>+</sup>, 77), 507 ((M-CH<sub>3</sub>)<sup>+</sup>, 65).

Found: m/z 522.10788, Calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: M, 522.10720.

### Synthesis of 7-hydroxy-3,4-bis(5-methyl-2-phenyl-4-thiazolyl)-coumarin (**3O**).

To a solution of 3,4-bis(5-methyl-2-phenyl-4-thiazolyl)-7-methoxycoumarin (**2O**) (98.2 mg, 0.188 mmol, 1.00 eq) in anhydrous dichloromethane (8 mL) was added an excess of boron tribromide (1.50 mL, 15.8 mmol, 84.0 eq) at -78 °C under a N<sub>2</sub> atmosphere. The resulting solution was stirred at room temperature for 3 days. The reaction was quenched by adding water at 0 °C and the resultant mixture was extracted with dichloromethane. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the drying agent filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate / hexane (30 %) as the eluent to give 32.1 mg

(0.0631 mmol) of **3O** as a white solid in 34% yield.

Mp 105-109 °C.

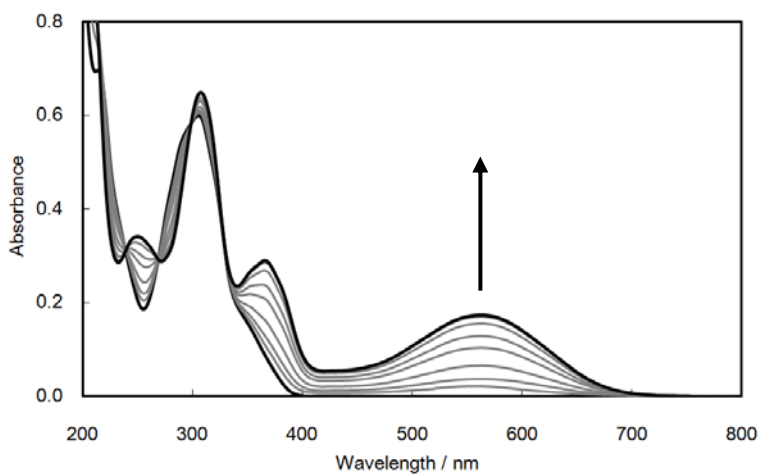
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ/ppm 2.22 (3H, s), 2.33 (3H, s), 6.70 (1H, dd, J/Hz=8.7, 2.4), 6.79 (1H, d, J/Hz=2.4), 7.10 (1H, d, J/Hz=8.7), 7.26-7.43 (6H, m), 7.69-7.72 (2H, m), 7.83-7.86 (2H, m), 8.63 (1H, brs). (**Fig. S26**).

IR (neat) v/cm<sup>-1</sup> 3284, 3062, 3022, 2920, 1720, 1693, 1614, 1599, 1569, 1462, 1220, 771.

LRMS (EI, 70 eV) m/z (rel intensity), 509 (M<sup>+</sup>, 4), 492 ((M-OH)<sup>+</sup>, 19), 449 ((M-60)<sup>+</sup>, 44), 367 ((M-142)<sup>+</sup>, 100), 278 ((M-231)<sup>+</sup>, 60)

Found: m/z 509.09923, Calcd for C<sub>29</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: M, 509.09881.

## ESI-2. Change in absorption spectra of **1**, **2** and **3** during photoirradiation

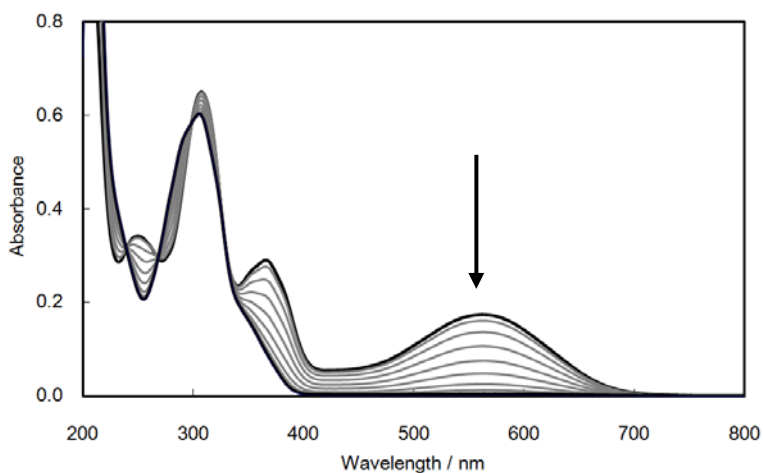


**Figure S1.** Change in absorption spectra from **10** to pss

Concentration / mol dm<sup>-3</sup>:  $2.70 \times 10^{-5}$  in hexane

Light intensity / mW cm<sup>-2</sup>: 0.165 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 3, 5, 8, 12

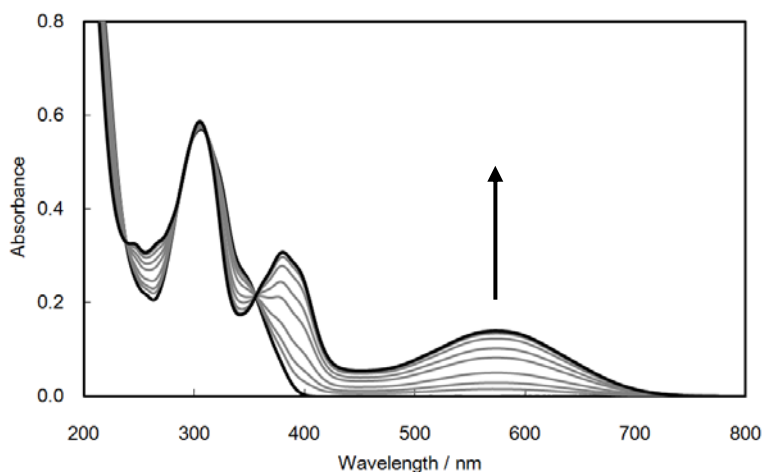


**Figure S2.** Change in absorption spectra from pss to **10**

Concentration / mol dm<sup>-3</sup>:  $2.70 \times 10^{-5}$  in hexane

Light intensity / mW cm<sup>-2</sup>: 3.18 (578 nm)

Irradiation time / min: 0, 1, 3, 6, 10, 15, 22, 30, 45, 75

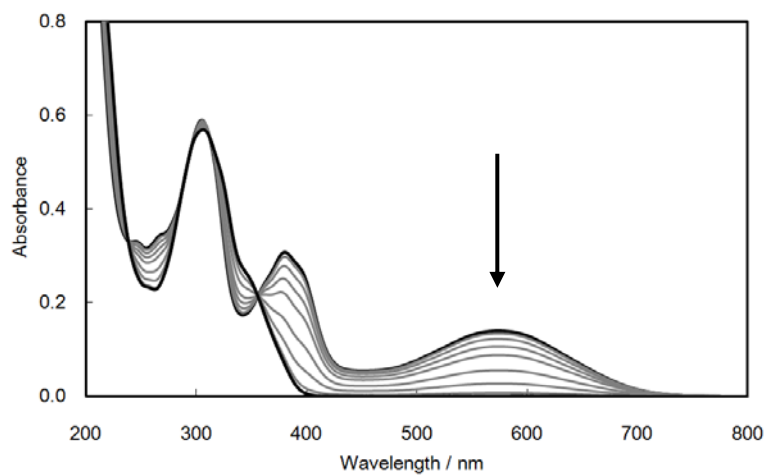


**Figure S3.** Change in absorption spectra from **2O** to pss

Concentration / mol dm<sup>-3</sup>:  $2.70 \times 10^{-5}$  in hexane

Light intensity / mW cm<sup>-2</sup>: 0.150 (313 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 3, 5, 8, 12, 15



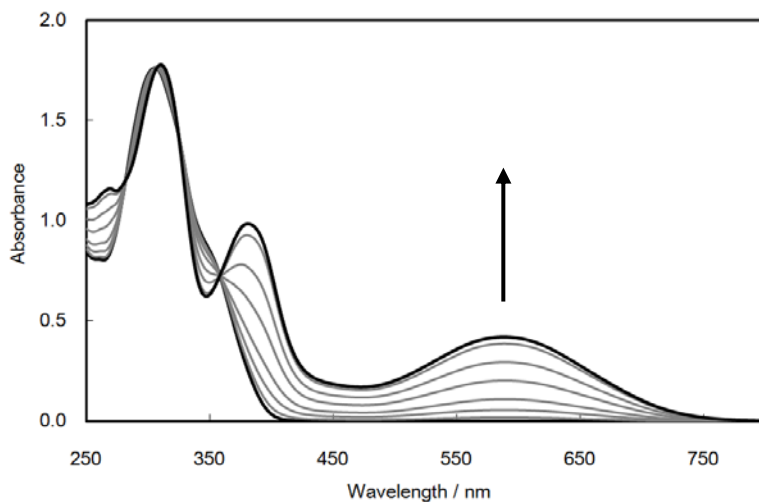
**Figure S4.** Change in absorption spectra from pss to **2O**

Concentration / mol dm<sup>-3</sup>:  $2.70 \times 10^{-5}$  in hexane

Light intensity / mW cm<sup>-2</sup>: 3.01 (578 nm)

Irradiation time / min: 0, 1, 3, 6, 10, 20, 35, 60, 105



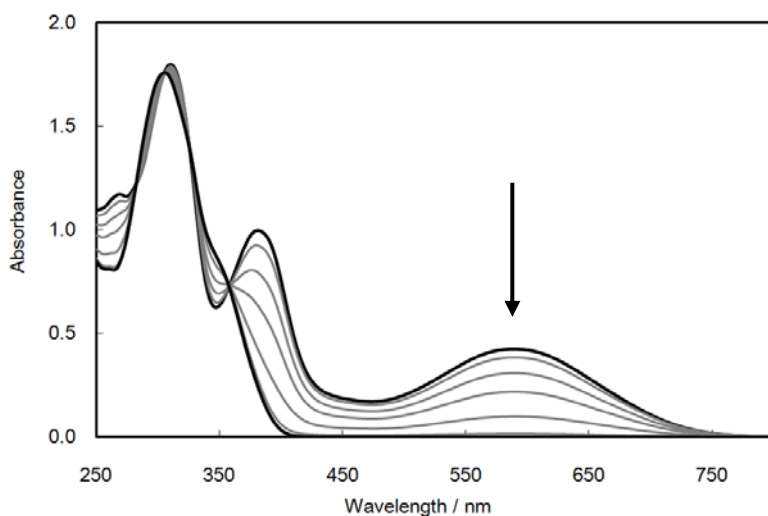


**Figure S5.** Change in absorption spectra from **3O** to pss

Concentration / mol dm<sup>-3</sup>: 6.16 x 10<sup>-5</sup> in CH<sub>2</sub>Cl<sub>2</sub>

Light intensity / mW cm<sup>-2</sup>: 0.414 (313 nm)

Irradiation time / min: 0, 1, 3, 6, 13, 24, 49, 100, 150



**Figure S6.** Change in absorption spectra from pss to **3O**

Concentration / mol dm<sup>-3</sup>: 6.16 x 10<sup>-5</sup> in CH<sub>2</sub>Cl<sub>2</sub>

Light intensity / mW cm<sup>-2</sup>: 8.57 (578 nm)

Irradiation time / min: 0, 1, 3, 6, 12, 24, 49

### ESI-3. Quantum yields of photoreactions of **1**, **2** and **3**

**Table S1.** Quantum Yields of the Photoreactions of **1**

Solvent	$E_T(30) /$ kcal mol <sup>-1</sup>	313 nm irradiation		Conversion /	578 nm irradiation
		$\Phi_{OC}$	$\Phi_{CO}$	%	$\Phi_{CO}$
MeCN	45.6	0.47	0.033	92	0.0031
AcOEt	38.1	0.30	0.019	93	0.0029
Toluene	33.9	0.40	0.033	93	0.0031
Hexane	31.0	0.44	0.031	92	0.0048

**Table S2.** Quantum Yields of the Photoreactions of **2**

Solvent	$E_T(30) /$ kcal mol <sup>-1</sup>	313 nm irradiation		Conversion /	578 nm irradiation
		$\Phi_{OC}$	$\Phi_{CO}$	%	$\Phi_{CO}$
MeCN	45.6	0.60	0.024	96	0.0026
Hexane	31.0	0.49	0.013	98	0.0035

**Table S3.** Quantum yields of the photoreaction and fluorescence of **3**

	<b>3O</b>				<b>3O<sub>anion</sub></b> <sup>a)</sup>				
	313 nm		Conversion/ %	578 nm $\Phi_{CO}$	405 nm		Conversion/ %	578 nm $\Phi_{CO}$	$\Phi_{FL}$ <sup>b)</sup>
	$\Phi_{OC}$	$\Phi_{CO}$			$\Phi_{OC}$	$\Phi_{CO}$			
CH <sub>2</sub> Cl <sub>2</sub>	0.033	0.00054	98	0.0030	0.17	0.036	>99	0.0010	0.019
CH <sub>3</sub> CN	0.17	0.0013	95	0.011	-	-	-	-	-
H <sub>2</sub> O-MeOH	-	-	-	-	0.36	0.00012	98.5	-	0.25

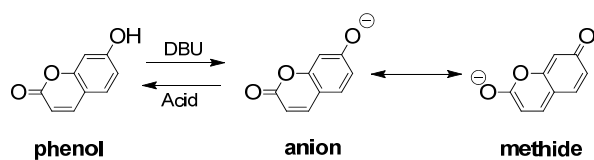
a) In order to generate **3O<sub>anion</sub>**, excess DBU was added when the photoreaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> and MeOH/10 mM sodium tetraborate buffer solution (pH 9.5) was used in H<sub>2</sub>O/MeOH. Conversion ratio was calculated from the fluorescence intensity

b) Excitation wavelength; 330 nm. Anthracene in EtOH was used as the fluorescence standard.

Tables S1, S2 and S3 show the quantum yields of photoreactions of **1**, **2**, and **3** in different solvents. Fluorescence quantum yields of **3O<sub>anion</sub>** are described in Table S3.

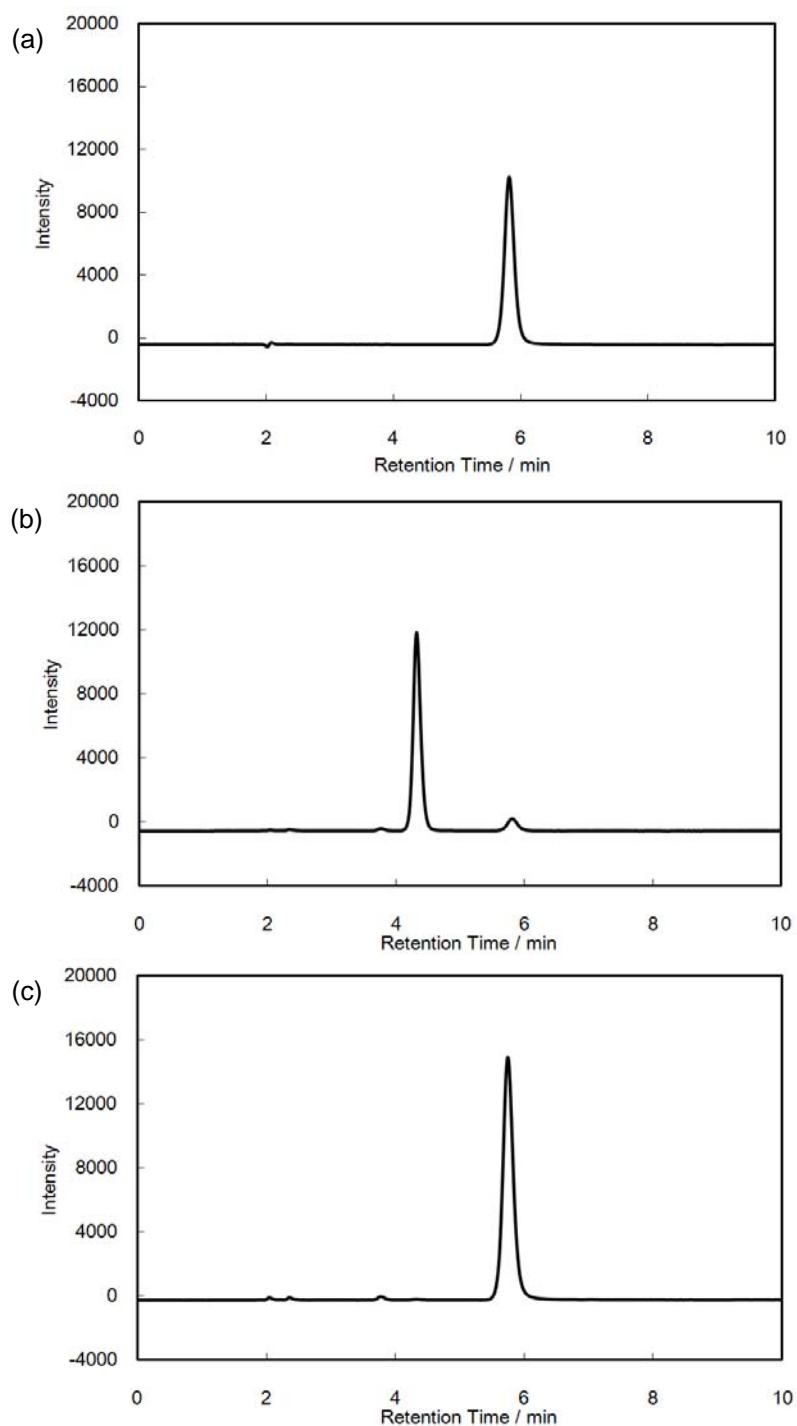
The photocyclozation quantum yields ( $\Phi_{OC}$ ) of **3O** and **3O<sub>anion</sub>** increased when the solvent polarity increased.

When DBU was added to **3O** in CH<sub>2</sub>Cl<sub>2</sub>, the phenolate anion was generated and the photocyclization occurred, and  $\Phi_{OC}$  of **3O<sub>anion</sub>** is larger than that of **3O**. However, when acetonitrile was used, it did not show photocyclization. This is in good accordance with the literature description<sup>1)</sup> that the phenolate anion of 7-hydroxycoumarin takes the quinone monomethide structure in polar solvents such as acetonitrile so that the hexatriene moiety which is necessary for electrocyclization is no longer existing. On the other hand, as **3C**, phenol structure generated in H<sub>2</sub>O/MeOH, was insoluble in this solvent, the quantum yields could not be determined.



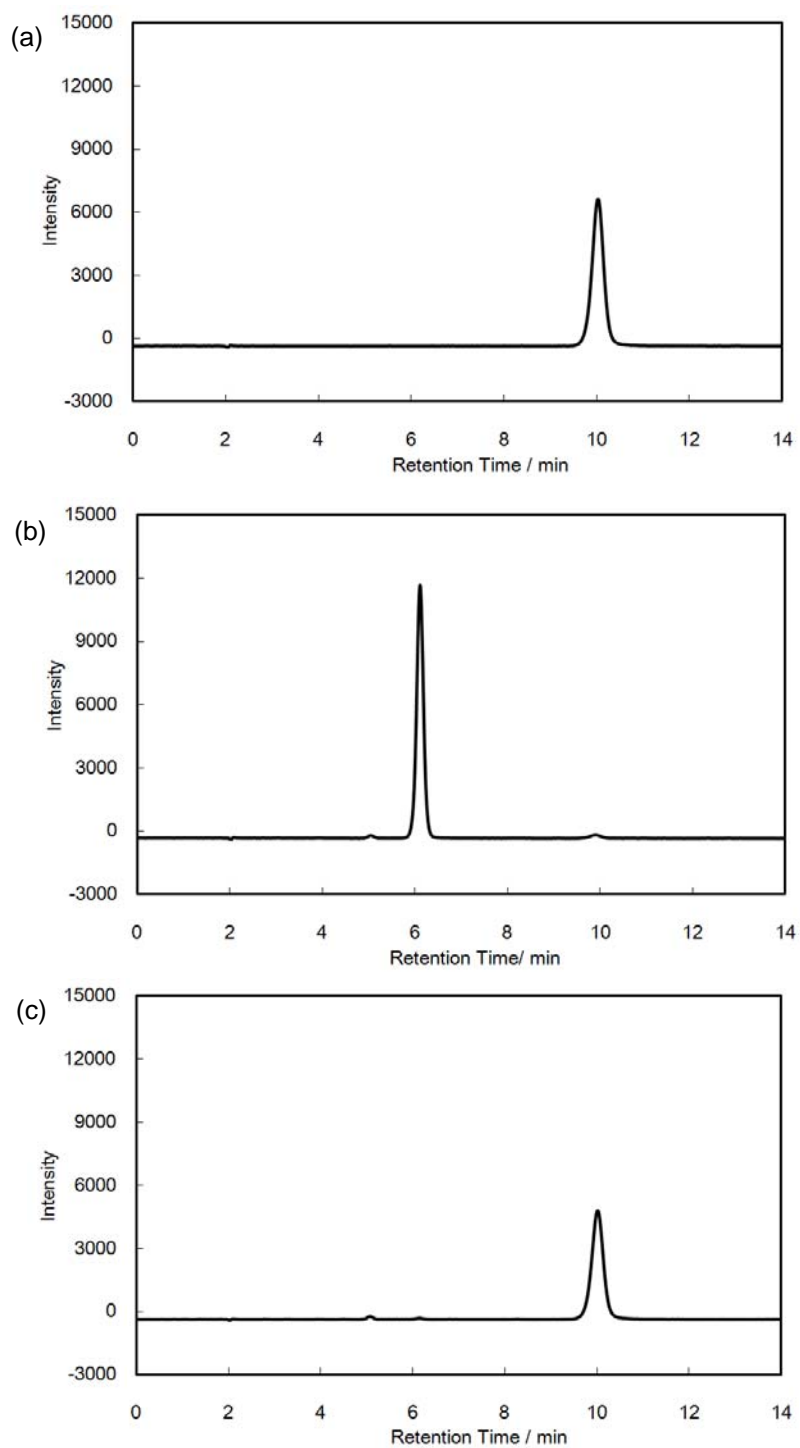
1) H. Mizoguchi, K. Kubo, T. Sakurai and H. Inoue, *Ber. Bunsenges. Phys. Chem.*, 1997, **101**, 1914-1920.

### ESI-4. HPLC chromatograms of **1**, **2** and **3** during photoirradiation



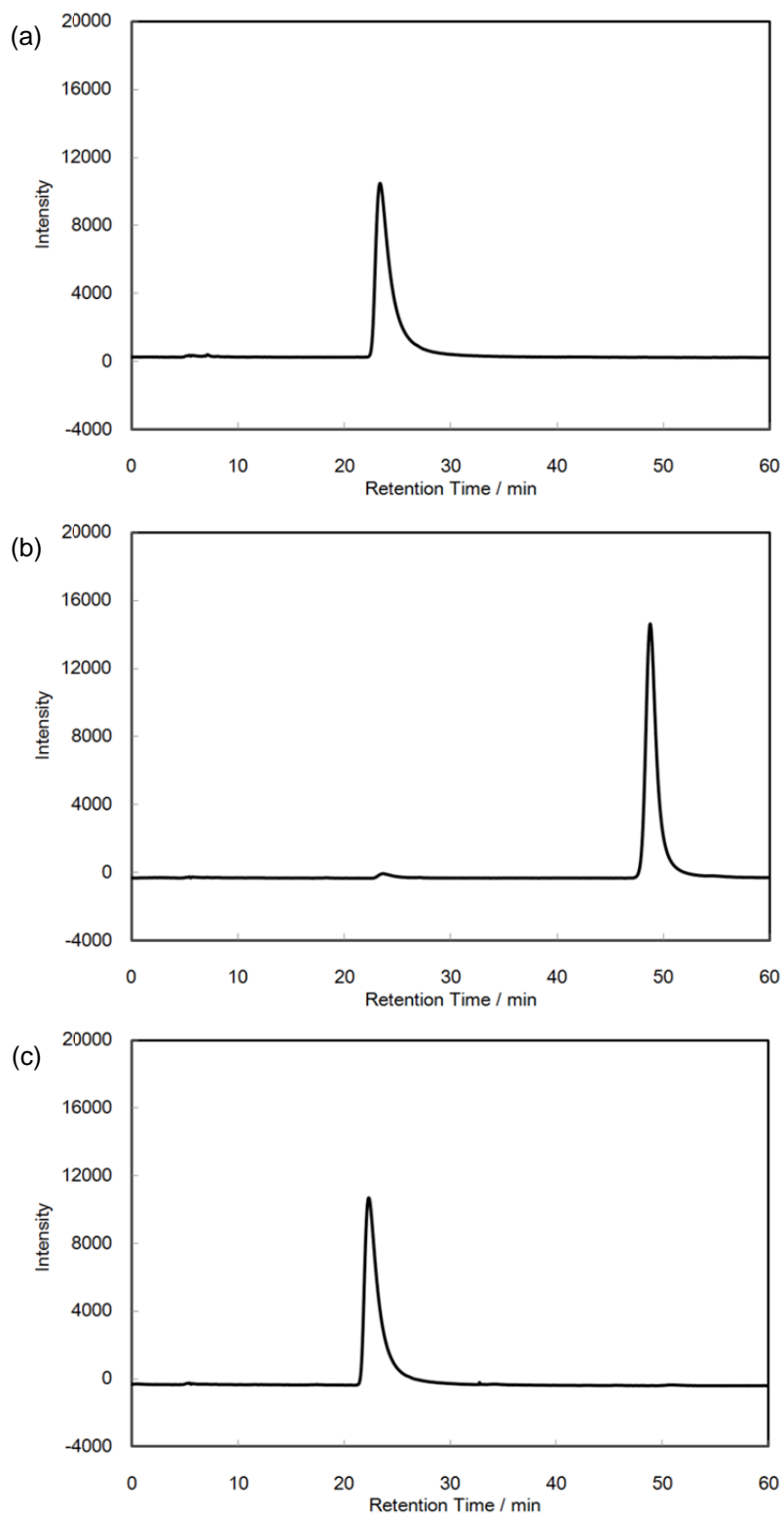
**Figure S7.** HPLC chromatograms of **1** in hexane.

Wakosil 5SIL, 20 % ethyl acetate / hexane, 1.0 ml min<sup>-1</sup>, Detection wavelength: 269 nm  
(a) Before irradiation, (b) Pss at 313 nm and (c) Pss at 578 nm



**Figure S8.** HPLC chromatograms of **2** in hexane.

Wakosil 5SIL, 20 % ethyl acetate / *n*-hexane, 1.0 ml min<sup>-1</sup>, Detection wavelength: 314 nm  
(a) Before irradiation, (b) Pss at 313 nm and (c) Pss at 578 nm



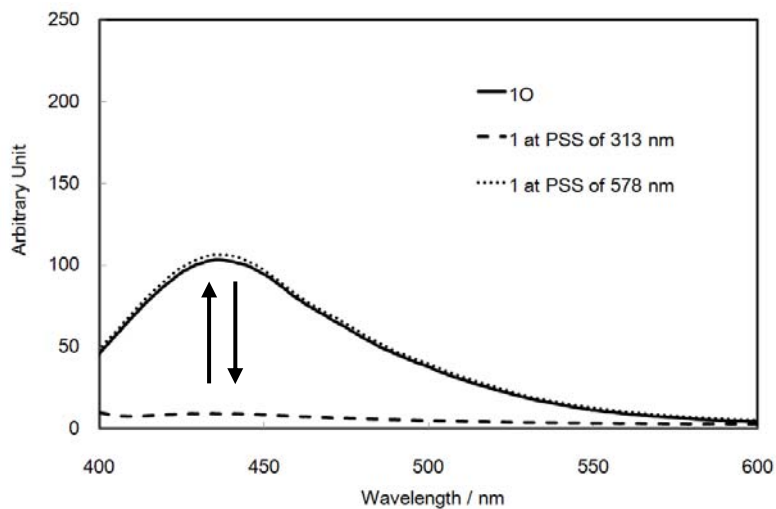
**Figure S9.** HPLC chromatograms of **3** in CH<sub>2</sub>Cl<sub>2</sub>.

WakoPak Navi C18-5, 80% acetonitrile / 20% sodium acetate buffer, 0.5 ml min<sup>-1</sup>.

Detection wavelength: 328 nm

(a) Before irradiation, (b) Pss at 313 nm and (c) Pss at 578 nm

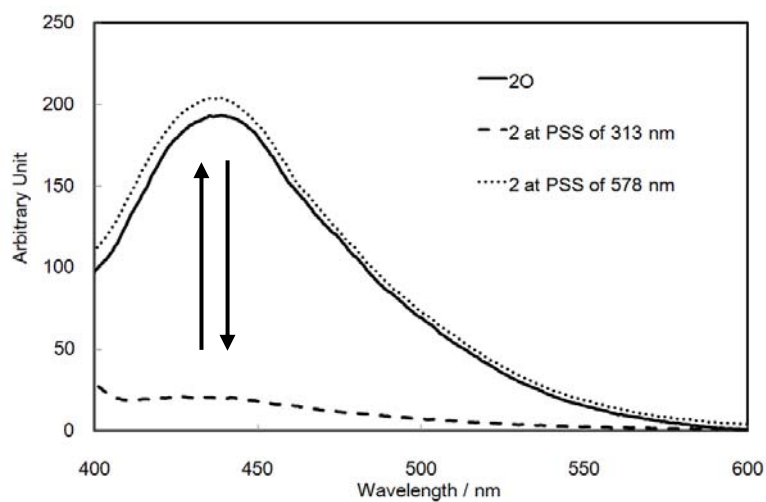
## ESI-5. Change in fluorescence spectra of **1** and **2** during photoirradiation



**Figure S10.** Change in fluorescence spectra of **1** upon successive irradiation of 313- and 578-nm lights.

Concentration / mol dm<sup>-3</sup>:  $3.20 \times 10^{-5}$  in hexane

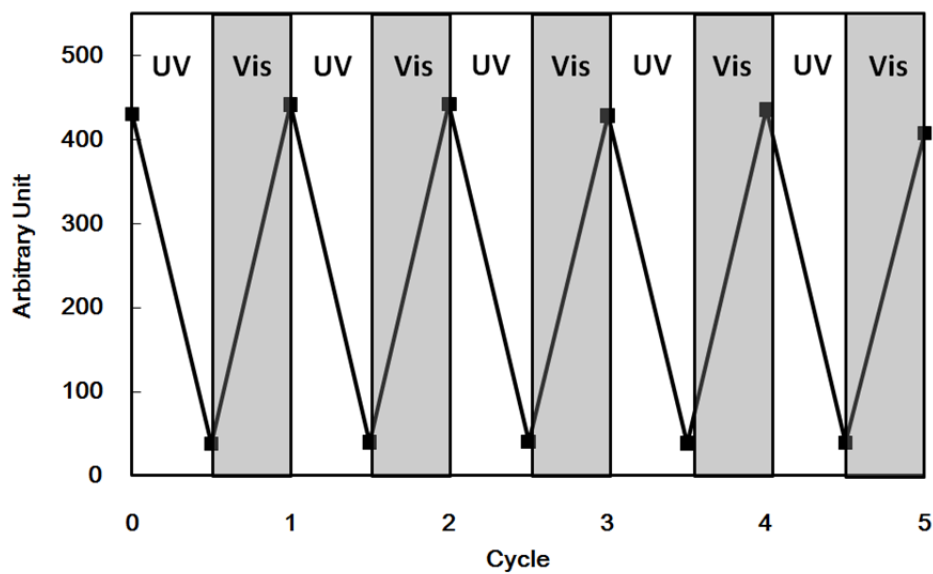
Excitation wavelength: 356 nm



**Figure S11.** Change in fluorescence spectra of **2** upon successive irradiation of 313- and 578-nm lights.

Concentration / mol dm<sup>-3</sup>:  $3.00 \times 10^{-5}$  in hexane

Excitation wavelength: 356 nm



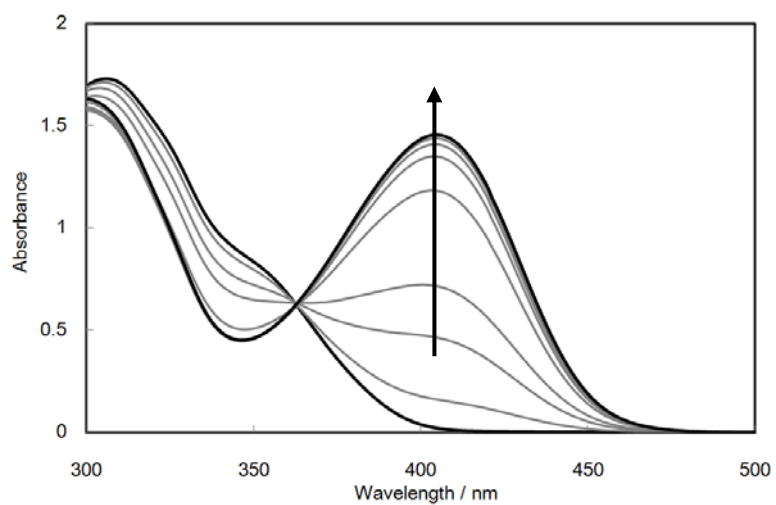
**Figure S12.** Change in fluorescence intensity of **2** detected at 436 nm upon repeated irradiation of 313- and 578-nm lights.

Concentration / mol dm<sup>-3</sup>: 3.00 x 10<sup>-5</sup> in hexane

Excitation wavelength: 356 nm



## ESI-6. Change in absorption spectra of **3** during acid-base titration



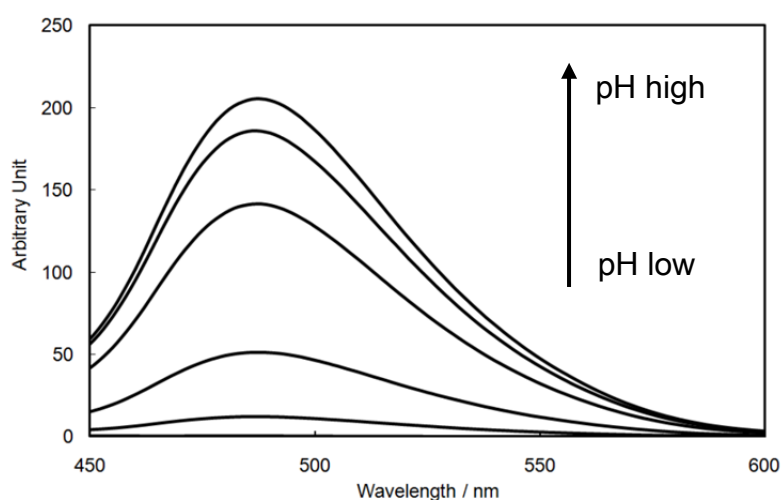
**Figure S13.** Change in absorption spectra of **3O** upon addition of DBU (0 to 12.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub>.

Concentration:  $6.2 \times 10^{-5} \text{ mol dm}^{-3}$

equivalence of DBU: 0, 0.1, 0.3, 0.5, 1, 2, 5, 8, 12

### ESI-7. Change in fluorescence spectra of **3** during acid-base titration: Determination of pKa

A solution of **3O** ( $5.10 \times 10^{-6} \text{ mol dm}^{-3}$ ) in  $\text{CH}_3\text{OH} / \text{H}_2\text{O}$  (1/2 v/v) containing  $\text{NaNO}_3$  (for adjusting ion strength;  $0.1 \text{ mol dm}^{-3}$ ) was prepared. The pH value of each solution was adjusted by adding aq.  $\text{NaOH}$  solution and hydrochloric acid. The fluorescence intensity detected at 487 nm was plotted on a graph with regard to the pH of each solution. A sigmoidal curve which fits best with the data obtained was searched using KaleidaGraph nonlinear regression analysis program (Synergy Software, Reading, PA, USA) to determine the pKa value.<sup>1)</sup>



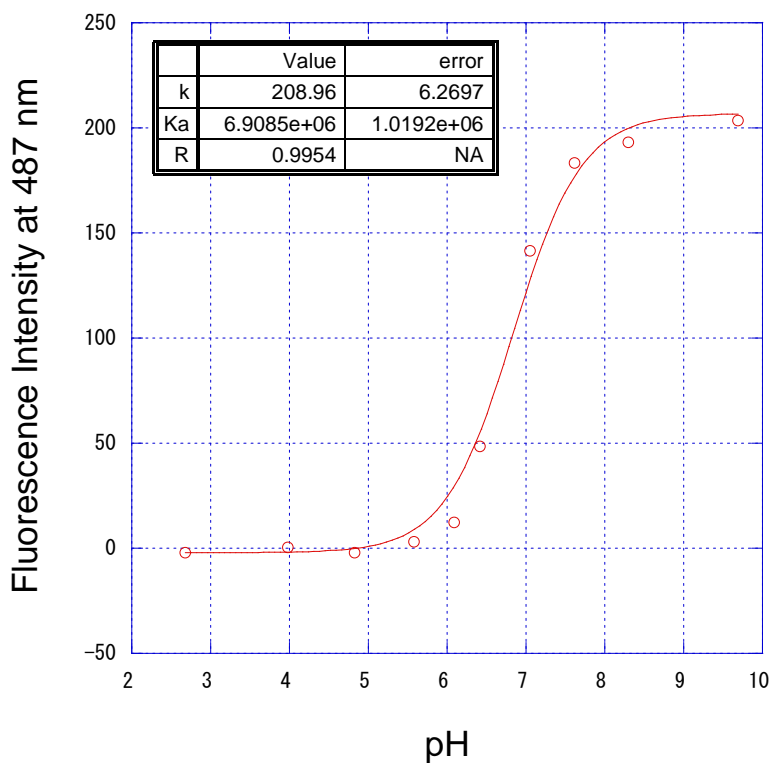
**Figure S14.** Fluorescence spectral change of **3O** at different pH values

Concentration /  $\text{mol dm}^{-3}$ :  $5.1 \times 10^{-6}$

Solvent:  $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:2$  (containing  $0.1 \text{ mol dm}^{-3}$  aq.  $\text{NaNO}_3$ )

Excitation Wavelength: 420 nm

pH of the solution: 2.64, 6.05, 6.38, 7.01, 7.58, 9.65



**Figure S15.** Change in fluorescence intensity of **3O** at 487 nm with the change of pH of the solution

Circles: Experimental. Curve: Calculated by the following equation.<sup>1)</sup>

$$F_{487} = F_{487}(2.6) + k / (K_a \cdot [H^+] + 1)$$

where  $F_{487}$  is the fluorescence intensity of **3O** at 487 nm at the designated pH,  $F_{487}(2.6)$  is the fluorescence intensity of **3O** at 487 nm at pH 2.6,  $K_a$  represents the dissociation constant,  $[H^+]$  stands for the concentration of proton,  $k$  expresses the value calculated by  $k = (\epsilon_{\text{anion}} \cdot \Phi_{\text{anion}} - \epsilon_{\text{phenol}} \cdot \Phi_{\text{phenol}})$ .  $\epsilon$  is the molar absorption coefficient at the excitation wavelength,  $\Phi$  is the fluorescence quantum yield at the excitation wavelength.

1) E. E. Conn and P. K. Stumpf, "Outlines of Biochemistry," 4th Ed., John Wiley and Sons, New York, 1976.

### ESI-8. Determination of fluorescence quantum yield

The excitation wavelength for the samples and the reference was 330 nm. Fluorescence spectra were calibrated by Rhodamine B. The relative quantum yields of the samples were obtained by comparing the area of the spectra of the sample and the reference. The fluorescence quantum yields were calculated with the following equation:

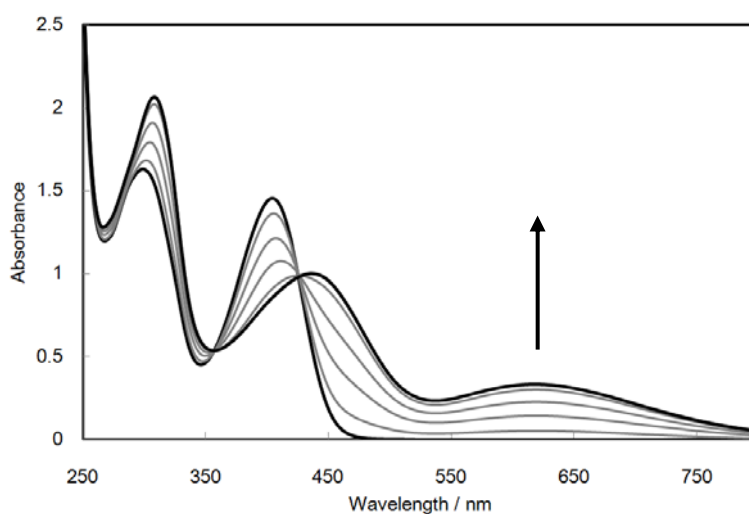
$$F_{\text{sample}} = F_{\text{ref}} (I_{\text{sample}}/I_{\text{ref}}) (A_{\text{ref}}/A_{\text{sample}}) (n_{\text{sample}}^2/n_{\text{ref}}^2)$$

where **F** is the quantum yield, **I** denotes the area of the fluorescence spectra, **A** represents the absorbance at the excitation wavelength, and **n** stands for the refractive index of the solvent used.

Anthracene ( $\phi = 0.30$  in EtOH<sup>1)</sup>) was used as the reference compound, which was used after recrystallization from EtOH.

1) M. Gunshefski, J. J. Santana, J. Stephenson and D. Winefordnert, *Appl. Spectrosc. Rev.*, 1992, **27**, 143-192.

### ESI-9. Change in absorption spectra of **3** during photoirradiation under basic condition

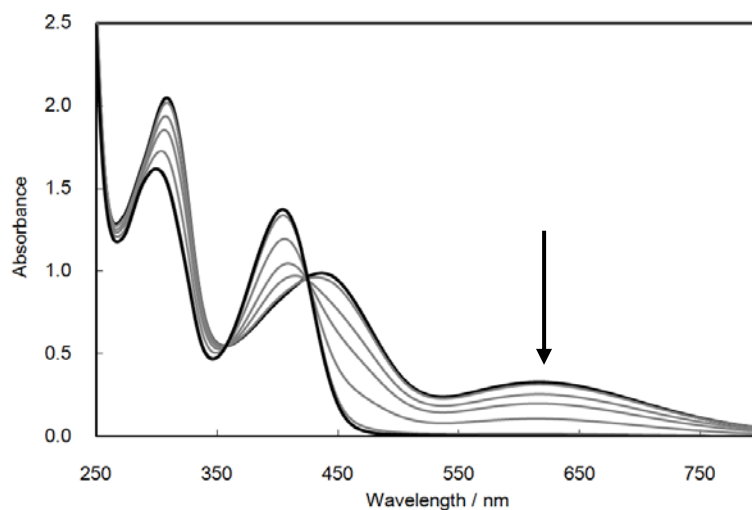


**Figure S16.** Change in absorption spectra of **30** to pss in  $\text{CH}_2\text{Cl}_2$  in the presence of 12.0 eq. DBU

Concentration /  $\text{mol dm}^{-3}$ :  $6.16 \times 10^{-5}$  in  $\text{CH}_2\text{Cl}_2$

Light intensity /  $\text{mW cm}^{-2}$ : 0.19 (405 nm)

Irradiation time / min: 0, 1, 3, 6, 12, 24, 40

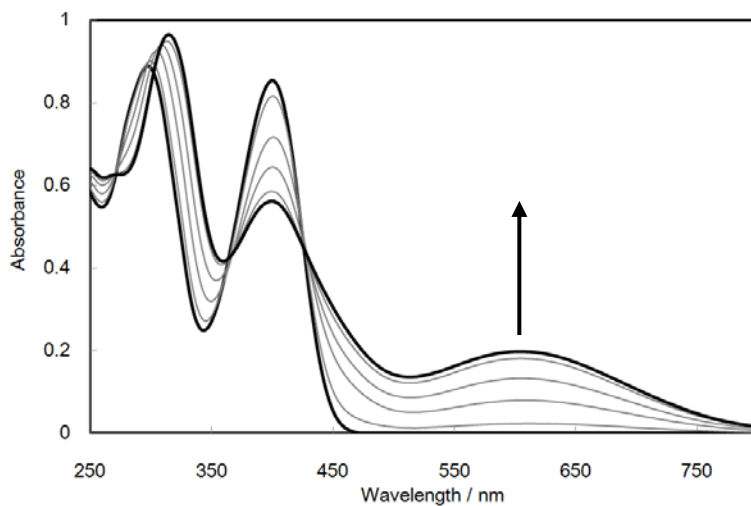


**Figure S17.** Change in absorption spectra of 405-nm pss to **30** in  $\text{CH}_2\text{Cl}_2$  in the presence of 12.0 eq. DBU

Concentration /  $\text{mol dm}^{-3}$ :  $6.16 \times 10^{-5}$  in  $\text{CH}_2\text{Cl}_2$

Light intensity /  $\text{mW cm}^{-2}$ : 5.49 (578 nm)

Irradiation time / min: 0, 3, 16, 30, 60, 130, 180



**Figure S18.** Change in absorption spectra of **30** to pss in CH<sub>3</sub>OH/buffer solution

Concentration / mol dm<sup>-3</sup>:  $4.38 \times 10^{-5}$

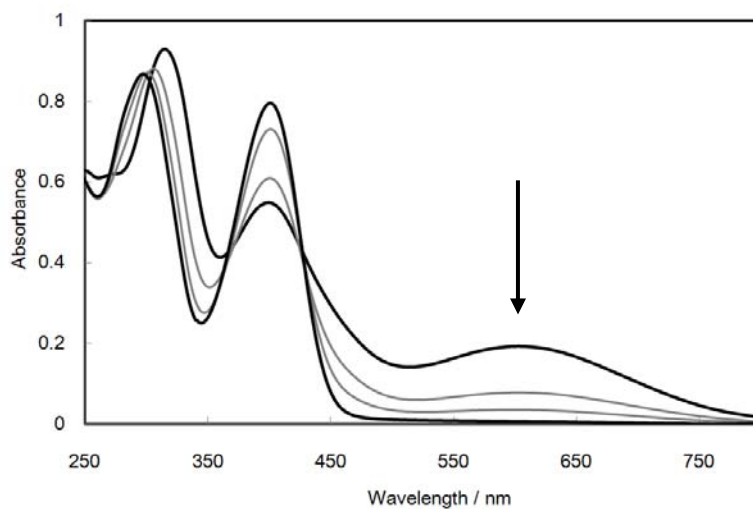
Solvent: CH<sub>3</sub>OH/Buffer solution = 2:1

Buffer solution: 10 mmol dm<sup>-3</sup> sodium tetraborate buffer

pH of the solution: 9.48

Light intensity / mW cm<sup>-2</sup>: 0.25 (405 nm)

Irradiation time / min: 0, 0.25, 0.5, 1, 2, 4, 7



**Figure S19.** Change in absorption spectra of 405-nm pss to **30** in CH<sub>3</sub>OH/buffer solution with >500-nm light irradiation

Concentration / mol dm<sup>-3</sup>:  $4.38 \times 10^{-5}$

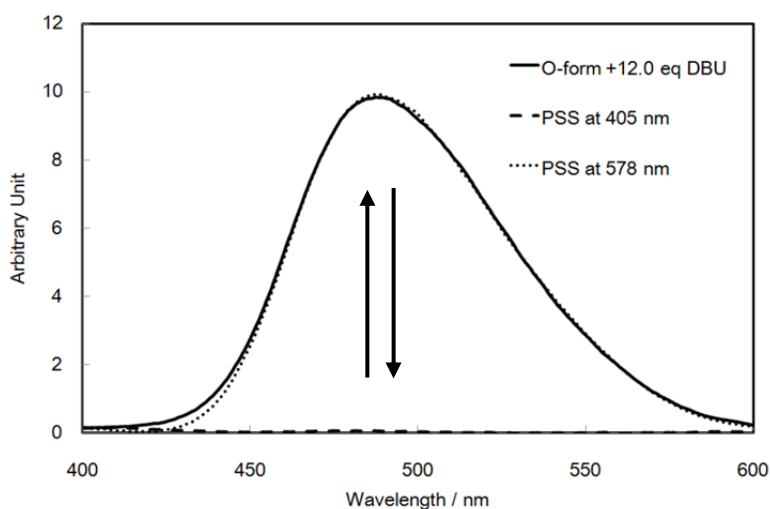
Solvent: CH<sub>3</sub>OH/Buffer solution = 2:1

Composition of the buffer solution: 10 m mol dm<sup>-3</sup> sodium tetraborate buffer

pH of the solution: 9.48

Irradiation time / min: 0, 31, 60, 120

## ESI-10. Change in fluorescence spectra of **3** during photoirradiation under basic condition

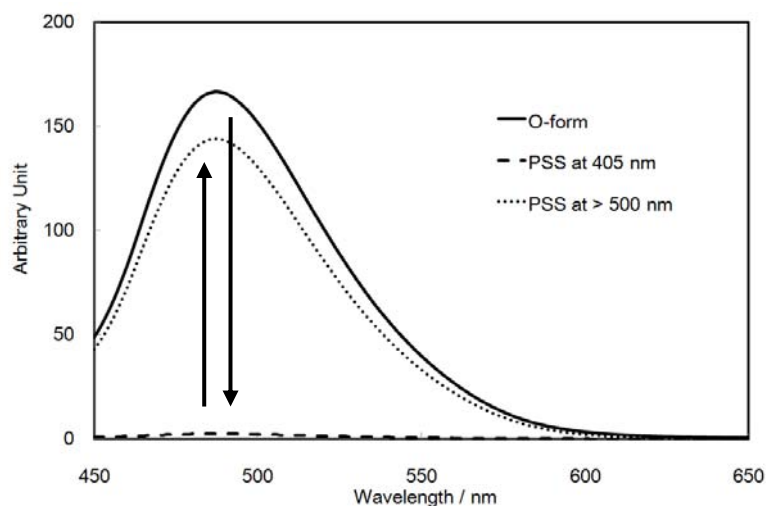


**Figure S20.** Change in fluorescence spectra of **3** in  $\text{CH}_2\text{Cl}_2$  in the presence of excess DBU upon successive irradiation with 405- and 578-nm lights.

Concentration /  $\text{mol dm}^{-3}$ :  $2.46 \times 10^{-6}$

Solvent:  $\text{CH}_2\text{Cl}_2$

Excitation wavelength: 330 nm



**Figure S21.** Change in fluorescence spectra of **3** under basic condition upon successive irradiation with 405- and >500-nm lights.

Concentration /  $\text{mol dm}^{-3}$ :  $2.75 \times 10^{-6}$

Solvent:  $\text{CH}_3\text{OH}/\text{Buffer solution} = 2:1$

Composition of the buffer solution:  $10 \text{ m mol dm}^{-3}$  sodium tetraborate buffer

pH of the solution: 9.51

Excitation wavelength: 420 nm





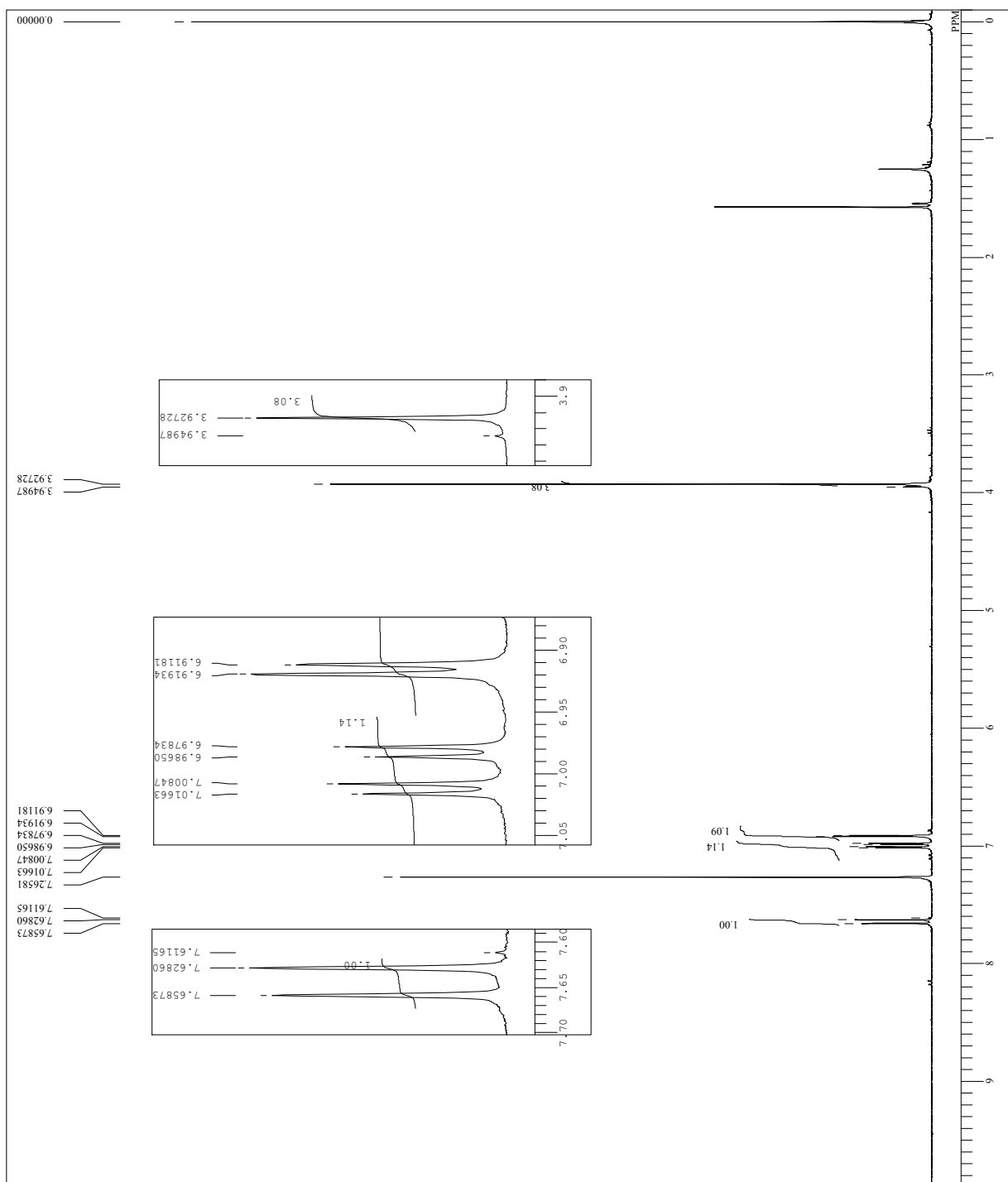
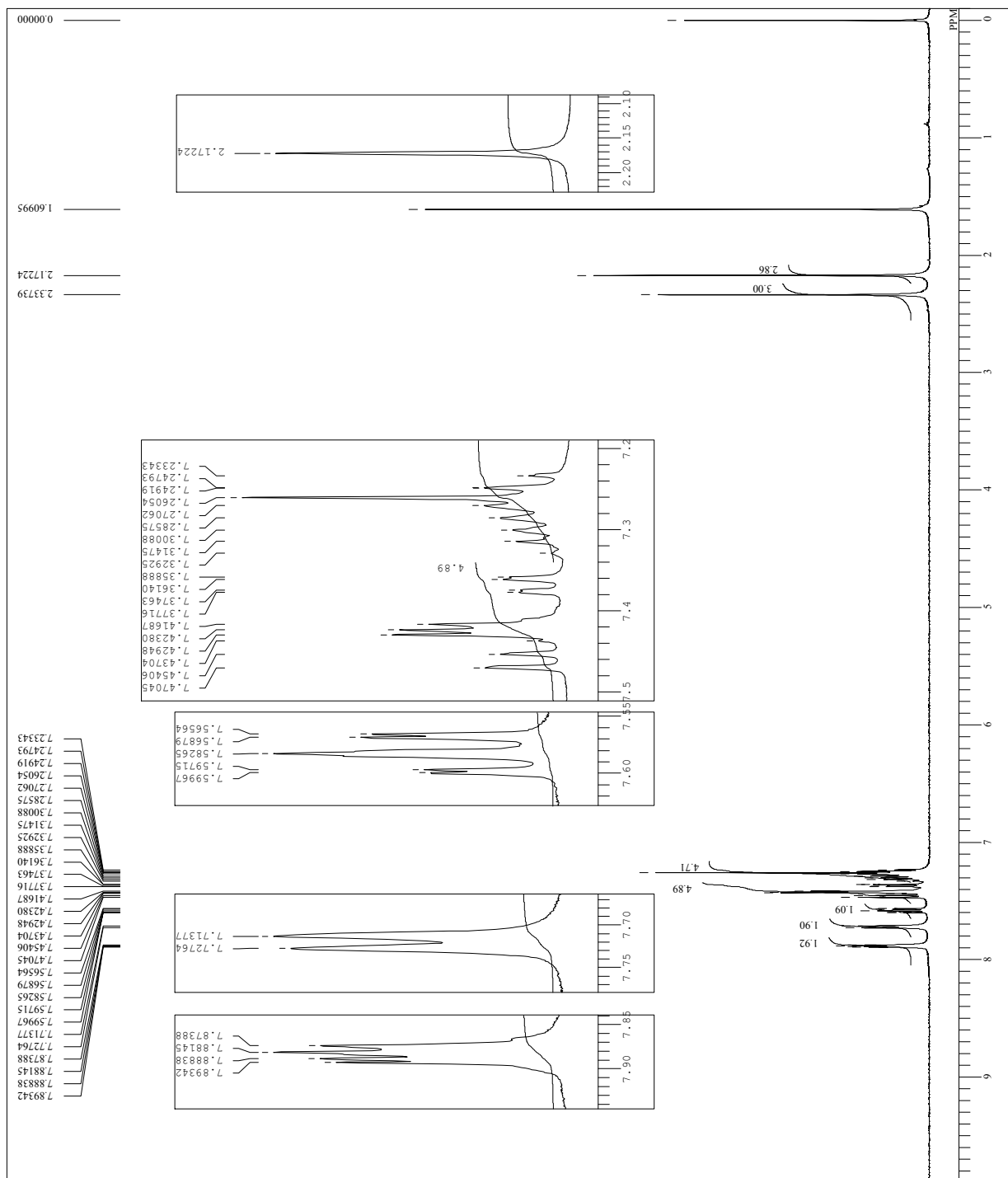
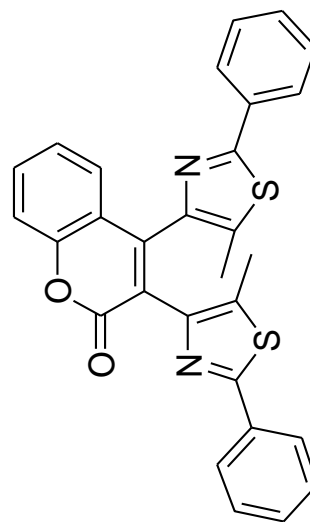


Fig. S23 <sup>1</sup>H NMR spectrum of compound **5** (300 MHz, CDCl<sub>3</sub>, TMS)



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PULPROG zgpg30  
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OBSF2 3.08 KHz  
OBSF3 51 Hz  
OBSF4 51 Hz  
OBSF5 51 Hz  
FREQU 10320.88 Hz  
SCANS 8  
ACQTM 0.0000 sec  
PD 0.0000 sec  
PWL 10.00 usec  
IRNUC  
CTEMP 24.8 c  
SLVNT CDCl3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 512



**10**

Fig. S24 <sup>1</sup>H NMR spectrum of compound **10** (500 MHz, CDCl<sub>3</sub>, TMS)

DPLE Ii-ka.hosoi.als  
COMPT User:YokoyamaYasushi\_lab  
DIR C:\Users\Yasushi\Documents\NMRPC  
DATE 11/11/11  
EXNM00 7430  
OBRO 300.13 MHz  
OBSET 1.89 KHz  
OBSF 10.00 Hz  
POINT 32768  
FREQ 6172.84 Hz  
SCANS 128  
ACQTM 5.3085 sec  
PD 1.0000 sec  
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IRNUC 20.9 c  
CLVNT CDCl3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 1024

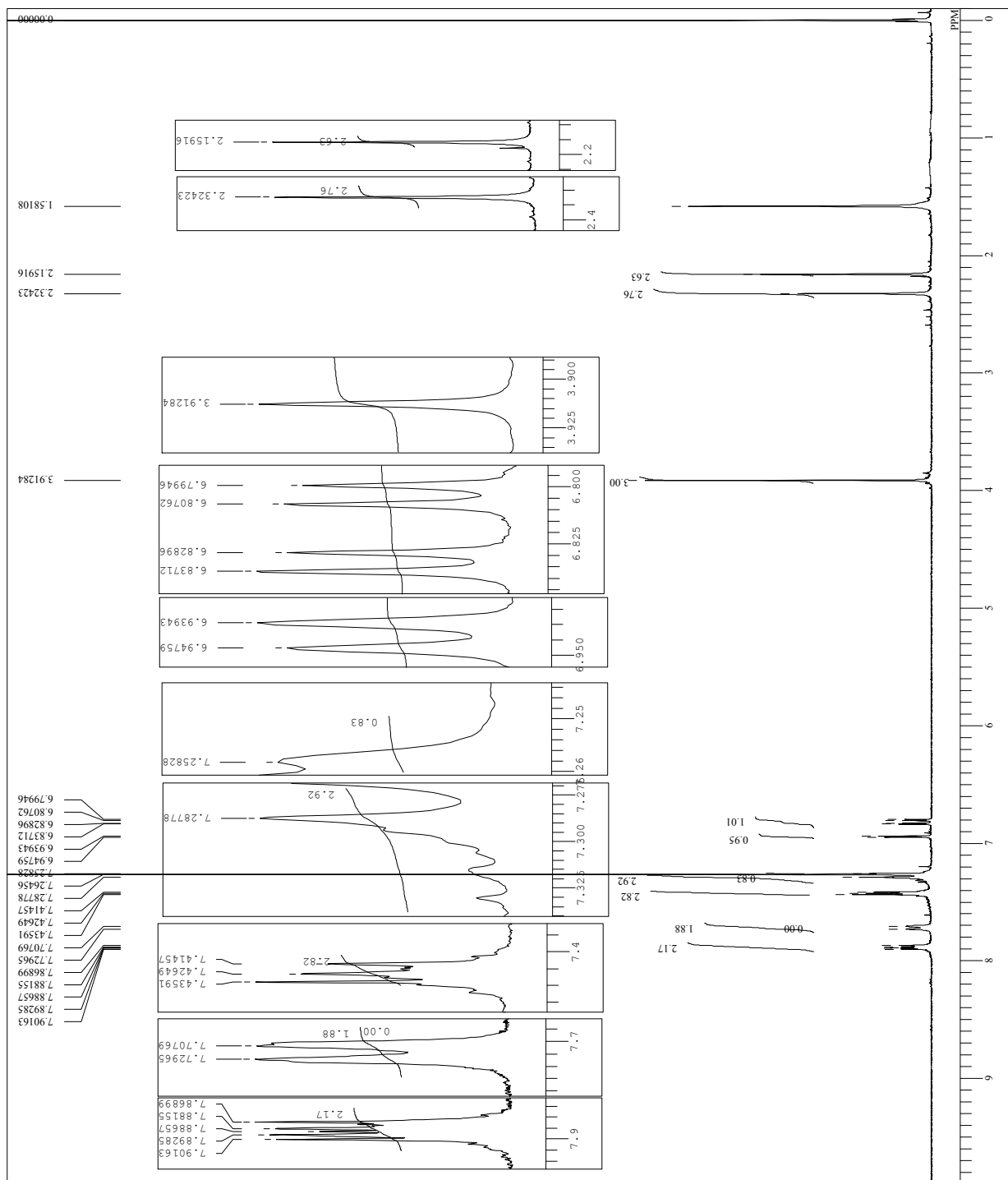


Fig. S25 <sup>1</sup>H NMR spectrum of compound **20** (300 MHz, CDCl<sub>3</sub>, TMS)

