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Electronic Supplementary Information

Solvent-Dependent Dual-Mode Photochromism between T- and P-types in a Dipyrrinone Derivative

Yoko Sakata,* Satomi Fukushima, Shigehisa Akine, and Jun-ichiro Setsune

* To whom correspondence should be addressed.

E-mail: sakata@se.kanazawa-u.ac.jp

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Experimental;

Materials and methods

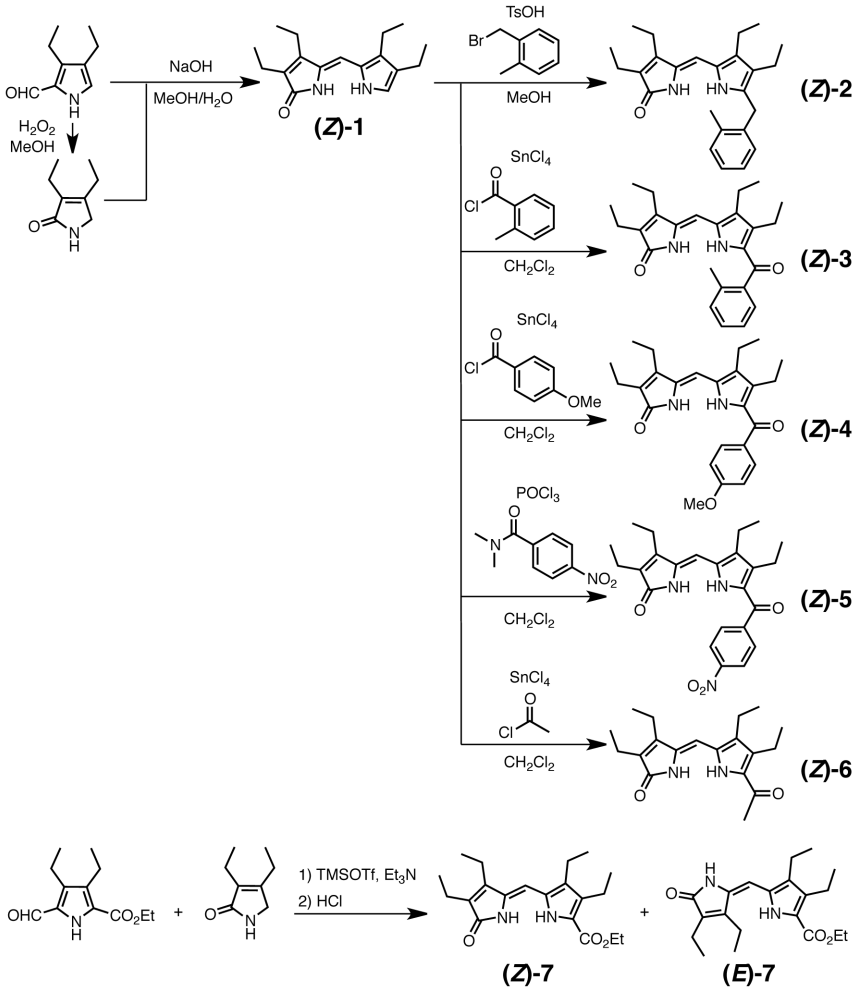
Reagents and solvents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 (500 and 125 MHz). Chemical shifts were referenced with respect to $(CH_3)_4Si$ (0 ppm) for ^{1}H and $CDCl_3$ (77.16 ppm) for ^{13}C as an internal standard. The UV-visible spectra were measured on a JACSO V-670 UV/VIS/NIR spectrometer equipped with a JASCO ETC-717 temperature/stirring controller. ESI-TOF mass spectra were recorded on an LTQ Orbitrap Discovery (Thermo Fischer Scientific). Photoirradiation for the sample solutions was performed with a 300W xenon lamp (Asahi spectra) equipped with a 400 nm or 280 nm optical filter at room temperature. For the photoswitching experiments, a 150W xenon lamp with an optical filter was used. For every cycle, the sample was irradiated with 400 nm and 280 nm lights for 30 min at room temperature.

Calculation details

We employed density functional theory (DFT) calculations to optimize the ground state geometries of (*Z*)-**7** and (*E*)-**7** using the hybrid density functional B3LYP with the 6-311G(d,p) basis set. At the optimized geometries, time-dependent (TD) DFT calculations on the B3LYP/6-31G(d,p) level were carried out to simulate the absorption spectra. All the calculations were carried out using the Gaussian09 program package[1] and the resulting theoretical spectra were drawn using Gausssum ver.2.2.[2]

Procedure for the synthesis of dipyrrinone derivatives;

3,4-Diethyl-2-formylpyrrole,[3] 3,4-diethyl-3-pyrrolin-2-one,[4] 2,3,7,8-tetraethyldipyrrinone (**1**),[5] and ethyl 3,4-diethyl-5-formylpyrrole-2-carboxylate[6] were prepared according to the procedure previously reported. Dipyrrinone derivatives were synthesized as outlined in Scheme S1.



Scheme. S1.

Synthesis of (*Z*)-2[7]

To a solution of 2,3,7,8-tetraethyldipyrrinone (**1**) (80.0 mg, 0.29 mmol) in dry methanol (80 mL) were added α-bromo-*o*-xylene (575 μL, 4.32 mmol) and *p*-toluenesulfonic acid monohydrate (80 mg, 0.46 mmol). The reaction mixture was stirred at 40 °C for 24 h under an argon atmosphere. After being cooled to room temperature, the resulting dark brown reaction mixture was concentrated to remove methanol. The residue was poured into water (100 mL) and extracted with dichloromethane (50 mL × 3), and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was removed, the crude material was purified by

silica gel column chromatography (CH_2Cl_2/MeOH = 1:0 - 50:1), followed by washing with hexane and dried in vacuo to obtain **(*Z*)-2** (61.3 mg, 0.16 mmol, 56%) as a yellow solid. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 10.98 (br, 1H), 10.24 (br, 1H), 7.14-6.95 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.14 (s, 1H), 4.10 (s, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.51 (q, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.25 (q, *J* = 7.6 Hz, 2H), 2.14 (q, *J* = 7.6 Hz, 2H), 1.19-1.15 (m, 6H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 173.78, 147.85, 138.19, 135.95, 132.94, 131.98, 129.95, 128.74, 128.62, 127.36, 126.20, 126.15, 123.15, 122.10, 101.26, 30.49, 19.90, 18.00, 17.98, 17.46, 17.24, 16.84, 16.02, 15.75, 14.26. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 377.2596, $C_{25}H_{33}N_2O$ requires 377.2587, $[M + Na]^+$ 399.2415, $C_{25}H_{32}N_2ONa$ requires 399.2407.

Synthesis of (*Z*)-3[7]

A solution of 2-methylbenzoyl chloride (300 μL, 2.33 mmol) in dry dichloromethane 150 mL was introduced into a 200 mL two-necked flask equipped with a magnetic stirrer and argon inlet. The flask was cooled to 0 °C and argon was bubbled through the solution. After 20 min, tin tetrachloride (15 drops) was introduced. Subsequently, a solution of 2,3,7,8-tetraethyldipyrrinone **1** (80.0 mg, 0.29 mmol) in dry dichloromethane (10 mL) was added. The mixture was stirred for another 20 min at 0 °C. The mixture was stirred for 1.5 h at room temperature, and then it was poured into water. The mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was evaporated, the crude material was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 1:0 - 50:1), followed by alumina column chromatography (CH_2Cl_2/MeOH = 1:0 - 50:1) to obtain **(*Z*)-3** (65.1 mg, 0.17 mmol, 72%) as a yellow solid. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 9.49 (br, 1H), 8.71 (br, 1H), 7.35-7.32 (m, 2H), 7.25-7.21 (m, 2H), 5.96 (s, 1H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.50 (q, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.15 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.83 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 187.16, 173.20, 147.32, 140.35, 136.38, 135.63, 135.12, 133.89, 130.87, 130.65, 130.50, 130.08, 129.82, 127.12, 125.61, 96.37, 19.44, 17.99, 17.96, 17.58, 17.12, 16.29, 15.92, 15.39, 13.79. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 391.2388, $C_{25}H_{31}N_2O_2$ requires 391.2380, $[M + Na]^+$ 413.2208, $C_{25}H_{30}N_2O_2Na$ requires 413.2199.

Synthesis of (*Z*)-4[7]

4-Methoxybenzoyl chloride (287 μL, 20.8 mmol) in dry dichloromethane 150 mL was introduced into a 200 mL two-neck flask equipped with an argon inlet. The flask was cooled to 0 °C and argon was bubbled through the solution. After 20 min, tin tetrachloride (15 drops) was introduced. Subsequently, a solution of 2,3,7,8-tetraethyldipyrrinone (**1**) (56.9 mg, 0.21 mmol) in dry dichloromethane (10 mL) was added. The mixture was stirred for another 20 min at 0 °C. The mixture was stirred for 2 h at room temperature, then it was poured into water. The mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was removed, the crude material was purified by alumina chromatography (CH_2Cl_2/MeOH = 1:0 - 100:1). The residue was washed with hexane and dried in vacuo to obtain **(*Z*)-4** (60.2 mg, 0.15 mmol, 71%) as a yellow solid. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 9.39 (br, 1H), 8.80 (br, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.00 (s, 1H), 3.83 (s, 3H), 2.59-2.51 (m, 6H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.06 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 185.36, 173.72, 162.75, 147.66, 134.80, 133.99, 133.10, 132.57, 131.13, 130.59, 130.39, 128.95, 113.77, 97.48, 55.51, 18.45, 17.96, 17.68, 17.03, 16.48, 15.99, 15.45, 13.83. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 407.2335, $C_{25}H_{31}N_2O_3$ requires 407.2329, $[M + Na]^+$ 429.2154, $C_{25}H_{30}N_2O_3Na$ requires 429.2149.

Synthesis of (*Z*)-5[8]

N,*N*′-Dimethyl-*p*-nitrobenzamide (973 mg, 5.00 mmol) was dissolved in phosphoryl chloride (690 μL, 7.40 mmol) and the solution was stirred for 15 h under an argon atmosphere. The reaction mixture was then diluted with dichloroethane (10 mL), and 2 mL of the solution was added to a solution of 2,3,7,8-tetraethyldipyrrinone (**1**) (60.0 mg, 0.22 mmol) in dry dichloromethane (10 mL). After the reaction mixture was stirred at room temperature for 9 h, saturated aqueous potassium carbonate solution was added carefully and the two-phase mixture was stirred for 15 min at room temperature and then 3 h under reflux. After being cooled to room temperature, the mixture was extracted with dichloromethane (50 mL × 3), and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was removed, the crude material was purified by alumina column chromatography (CH_2Cl_2), followed by silica gel chromatography (CH_2Cl_2 - $CHCl_3$) to obtain **(*Z*)-5** (81.0 mg, 0.19 mmol, 87%) as an orange solid. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 9.82 (br, 1H), 9.65 (br, 1H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 6.01 (s, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.51 (q,

J = 7.6 Hz, 2H), 2.43 (q, *J* = 7.6 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.18 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 183.49, 174.07, 149.38, 148.11, 145.83, 135.84, 135.68, 133.35, 131.29, 131.10, 129.75, 129.51, 123.60, 97.26, 18.46, 17.94, 17.56, 17.00, 16.34, 16.00, 15.39, 13.81. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 422.2072, $C_{24}H_{28}N_3O_4$ requires 422.2074, $[M + Na]^+$ 444.1893, $C_{24}H_{27}N_3O_4Na$ requires 444.1894.

Synthesis of (*Z*)-6[9]

Anhydrous aluminum chloride (133 mg, 1.00 mmol) was suspended in dry dichloromethane (10 mL) and the mixture was cooled to 0 °C while the acetyl chloride (60 μL, 0.60 mmol) was added. The mixture was kept at 0 °C for an additional 10 min and a solution of 2,3,7,8-tetraethyldipyrrinone **1** (54.5 mg, 0.20 mmol) in dry dichloromethane (10 mL) was added in one portion. The solution was stirred at room temperature for 24 h. The reaction was monitored by TLC, which indicated some remaining **1** and therefore a mixture of aluminum chloride (500 mg, 3.75 mmol) and acetyl chloride (160 μL, 1.60 mmol) in dry dichloromethane (10 mL) was further added. After stirring for another 12 h at room temperature, the reaction mixture was poured into water and neutralized with saturated aqueous sodium hydrogen carbonate solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane (50 mL × 3), and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was evaporated, the crude material was purified by alumina column chromatography (CH_2Cl_2 - $CHCl_3$), followed by silica gel chromatography (CH_2Cl_2/MeOH = 1:0 - 100:1) to obtain **(*Z*)-6** (62.7mg, 0.20 mmol, >99%) as a yellow solid. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 9.61 (br, 1H), 9.13 (br, 1H), 5.97 (s, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H), 1.10 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 187.61, 173.57, 147.58, 135.31, 133.32, 133.23, 130.88, 130.13, 129.19, 96.88, 27.74, 18.74, 17.97, 17.54, 17.10, 16.49, 16.18, 15.47, 13.86. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 315.2070, $C_{19}H_{27}N_2O_2$ requires 315.2067, $[M + Na]^+$ 337.1885, $C_{19}H_{26}N_2O_2Na$ requires 337.1886.

Synthesis of (*Z*)-7 and (*E*)-7[10]

To a stirred solution of 3,4-diethyl-3-pyrrolin-2-one (250 mg, 1.80 mmol) and triethylamine (2.0 mL) in dry dichloromethane (10 mL) was added dropwise trimethylsilyl

trifluoromethanesulfonate (1.0 mL, 5.40 mmol) at 0 °C. After stirring for 15 min, a solution of ethyl 3,4-diethyl-5-formylpyrrole-2-carboxylate (420 mg, 1.80 mmol) in dry dichloromethane (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and poured into water. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was dissolved in tetrahydrofuran (50 mL) and hydrochloric acid (3 M, 2 mL) was added to the mixture, which was stirred at room temperature for 15 min. The reaction mixture was diluted with dichloromethane (50 mL) and poured into saturated aqueous sodium hydrogen carbonate solution (50 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (50 mL × 3) and the combined organic extract was dried over anhydrous sodium sulfate. After the solvent was evaporated, the crude material was purified by silica gel chromatography (CH_2Cl_2/MeOH = 1:0 - 100:1) to obtain **(*Z*)-7** (155 mg, 0.45 mmol, 25%) as a yellow solid and **(*E*)-7** (59.0 mg, 0.17 mmol, 9.5%) as a pale yellow solid, respectively.

(*Z*)-7; ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 8.88 (br, 1H), 7.88 (s, 1H), 5.96 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.51 (q, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 173.09, 161.00, 147.48, 135.45, 134.27, 133.47, 129.32, 127.83, 121.07, 96.96, 60.33, 18.29, 17.97, 17.59, 17.11, 16.44, 15.76, 15.41, 14.66, 13.80. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 345.2181, $C_{20}H_{29}N_2O_3$ requires 345.2173, $[M + Na]^+$ 367.2001, $C_{20}H_{28}N_2O_3Na$ requires 367.1992.

(*E*)-7; ^{1}H NMR (500 MHz, 293 K, $CDCl_3$) δ 8.62 (br, 1H), 7.23 (s, 1H), 6.12 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.44 (q, *J* = 7.6 Hz, 2H), 2.38 (q, *J* = 7.6 Hz, 2H), 2.32 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.09 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, 293 K, $CDCl_3$) δ 170.73, 161.29, 144.38, 139.22, 138.55, 133.83, 127.71, 126.31, 119.06, 101.20, 60.17, 19.17, 18.41, 17.79, 17.30, 15.98, 15.89, 14.63, 14.31, 13.66. HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 345.2173, $C_{20}H_{29}N_2O_3$ requires 345.2173, $[M + Na]^+$ 367.1992, $C_{20}H_{28}N_2O_3Na$ requires 367.1992.

NOESY spectrum of (*Z*)-7;

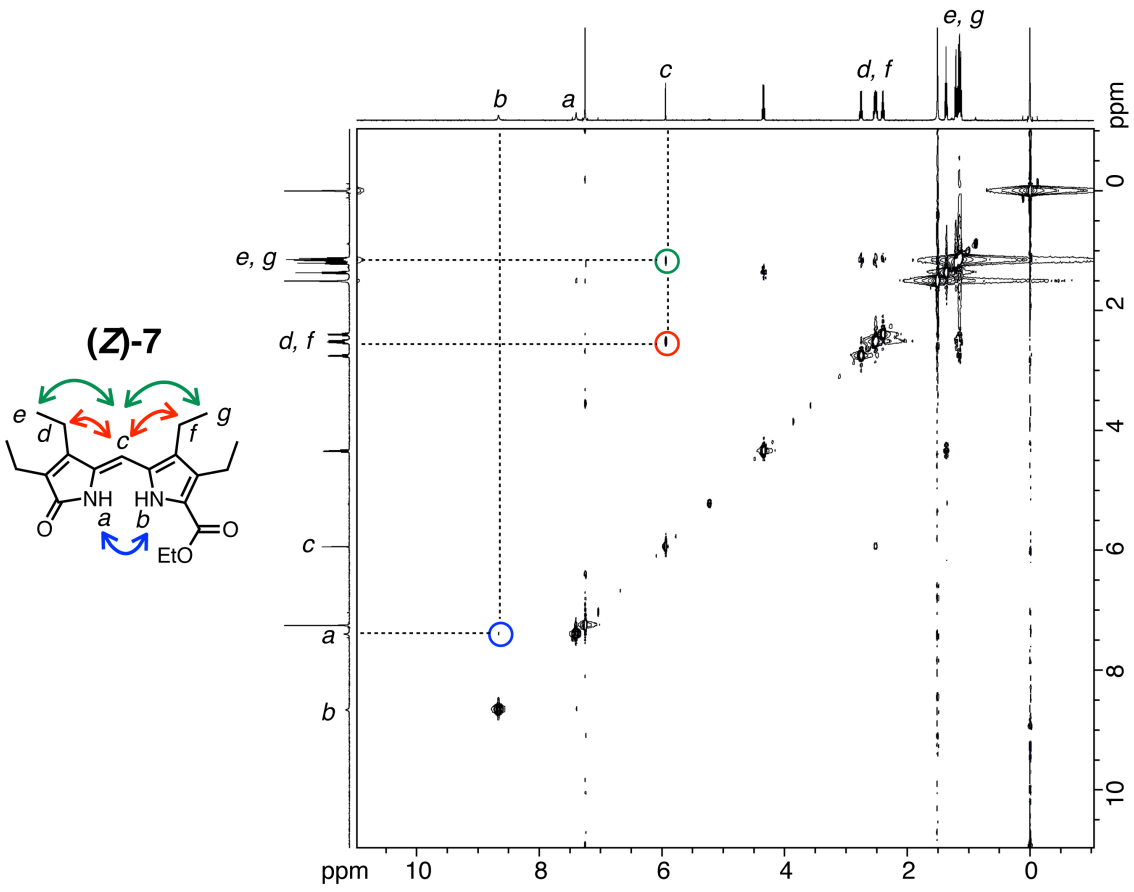


Fig. S1. NOESY spectrum of (*Z*)-**7**. Strong NOEs were observed between the dipyrrinone lactam NH (*a*) and pyrrole NH (*b*), and between meso CH (*c*) and methylene CH_2 (*d*, *f*) in the *Z* isomer, indicating that (Z)-**7** prefers the *syn* conformation.

NOESY spectrum of (*E*)-7;

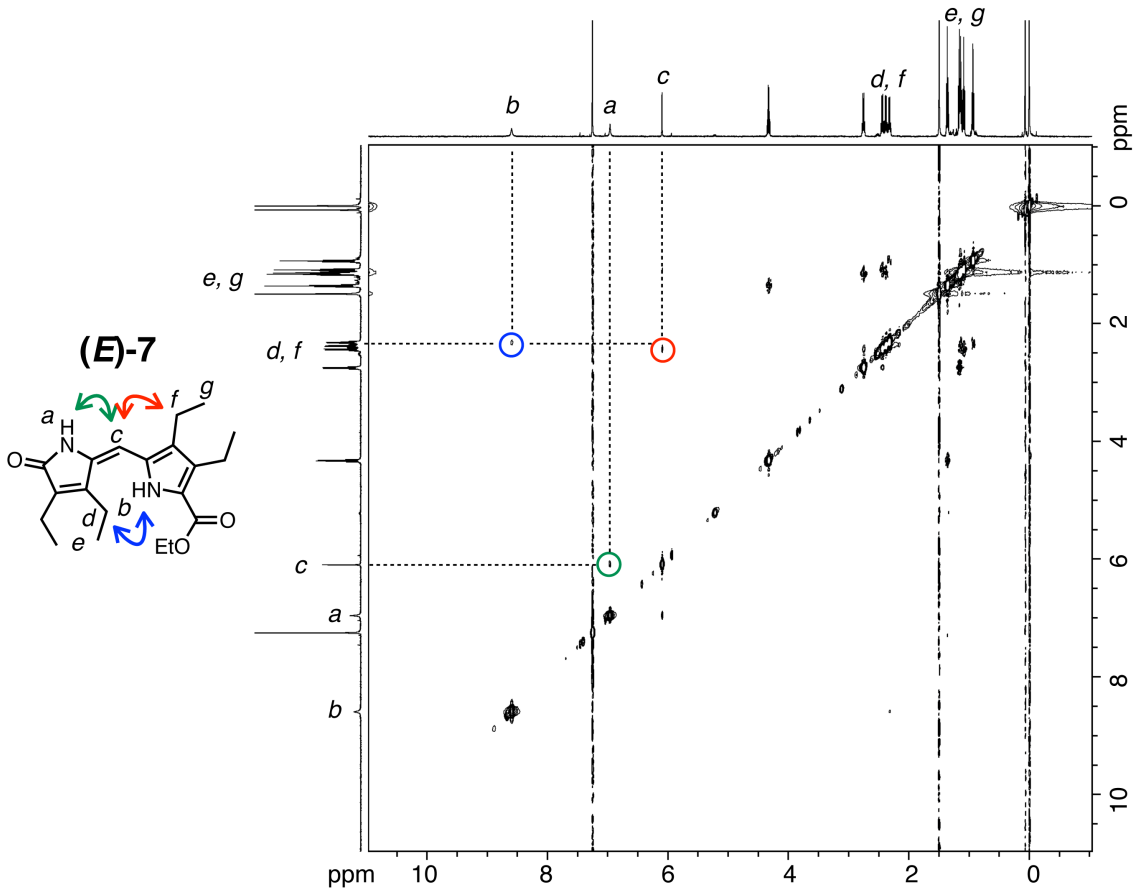


Fig. S2. NOESY spectrum of (*E*)-**7**. The *E*-isomer shows no NOE between NHs (*a*, *b*), whereas NOEs between lactam NH (*a*) and meso CH (*c*), and between pyrrole NH (*b*) and methylene CH_2 (*d*) were found.

UV-vis spectra of dipyrrinone derivatives in $CHCl_3$;

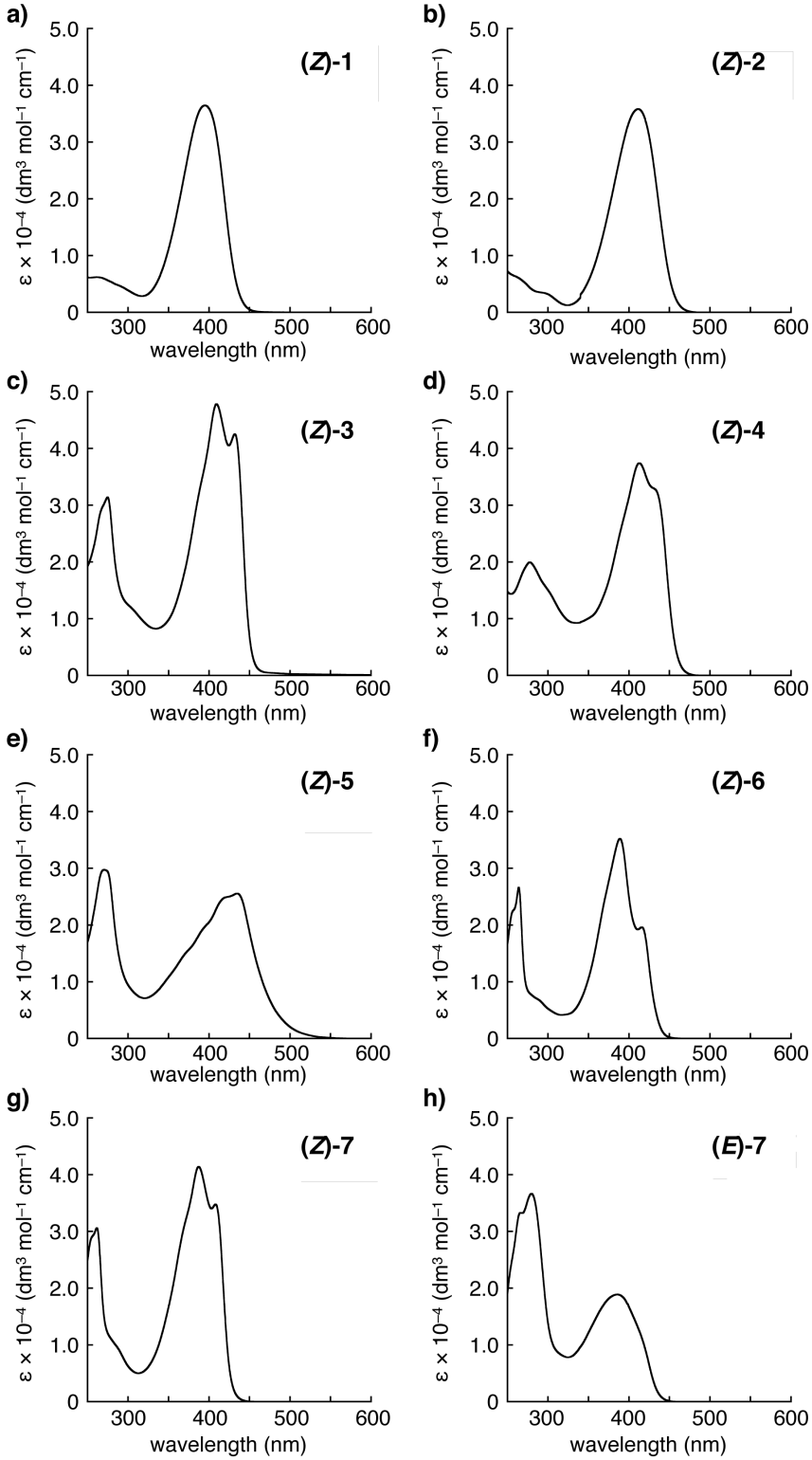


Fig. S3. UV-vis absorption spectra of dipyrrinone derivatives in chloroform. a) (*Z*)-**1**, b) (*Z*)-**2**, c) (*Z*)-**3**, d) (*Z*)-**4**, e) (*Z*)-**5**, f) (*Z*)-**6**, g) (*Z*)-**7**, h) (*E*)-**7**.

The molecular orbital plots of (*Z*)-7 and (*E*)-7;

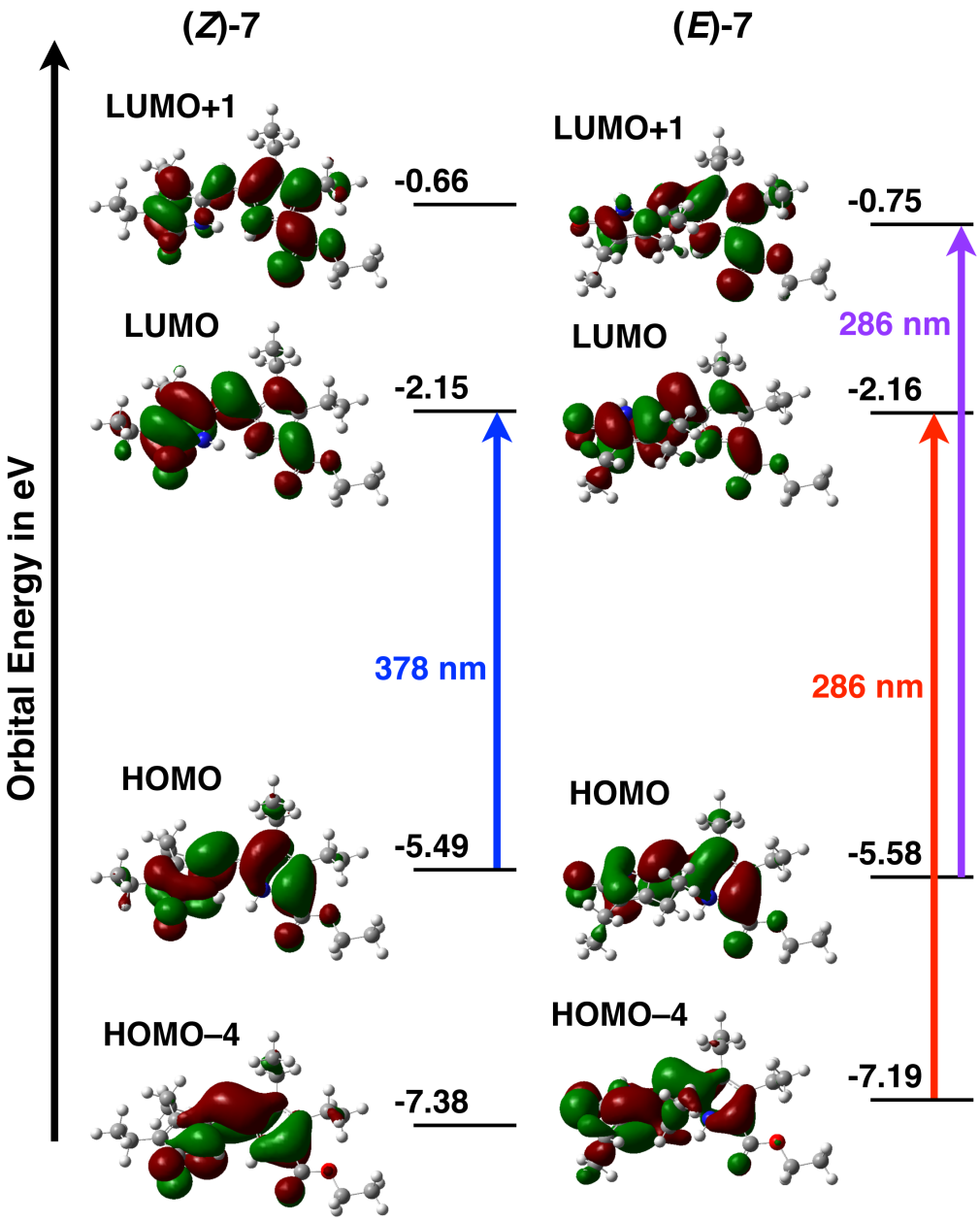


Fig. S4. The molecular orbitals of (*Z*)-**7** and (*E*)-**7** calculated at the B3LYP/6-311G(d,p) level of theory. According to the TD-DFT calculations, the most intense absorption band of (*Z*)-**7** at 378 nm is attributed to the HOMO → LUMO (99%) excitation. On the other hand, the absorption at UV region for (*E*)-**7** (286 nm) is mainly attributed to HOMO-4→LUMO (28%) and HOMO→LUMO+1 (56%) excitations.

Simulated absorption spectra of (*Z*)-7 and (*E*)-7;

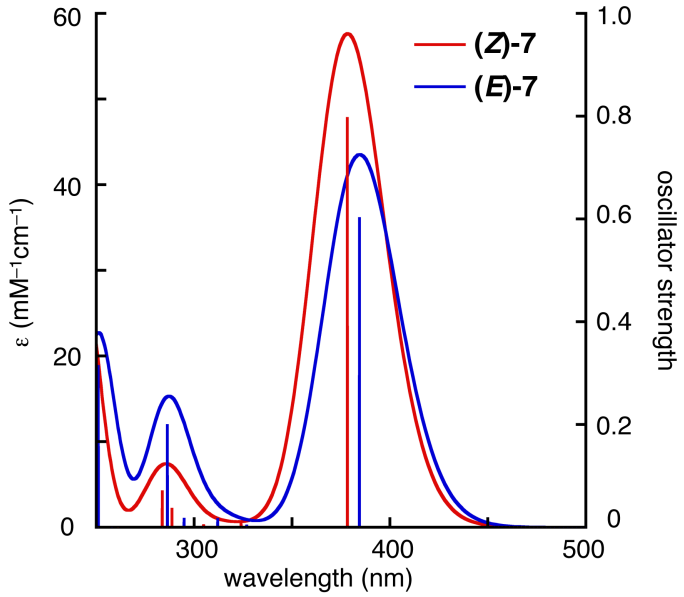


Fig. S5. Theoretical UV-vis absorption spectra calculated for (*Z*)-**7** and (*E*)-**7**. The bars indicate the oscillator strength of the transition calculated by TD-DFT.

Photoisomerization of (*Z*)-7 in $CDCl_3$ and thermal relaxation at 25 °C;

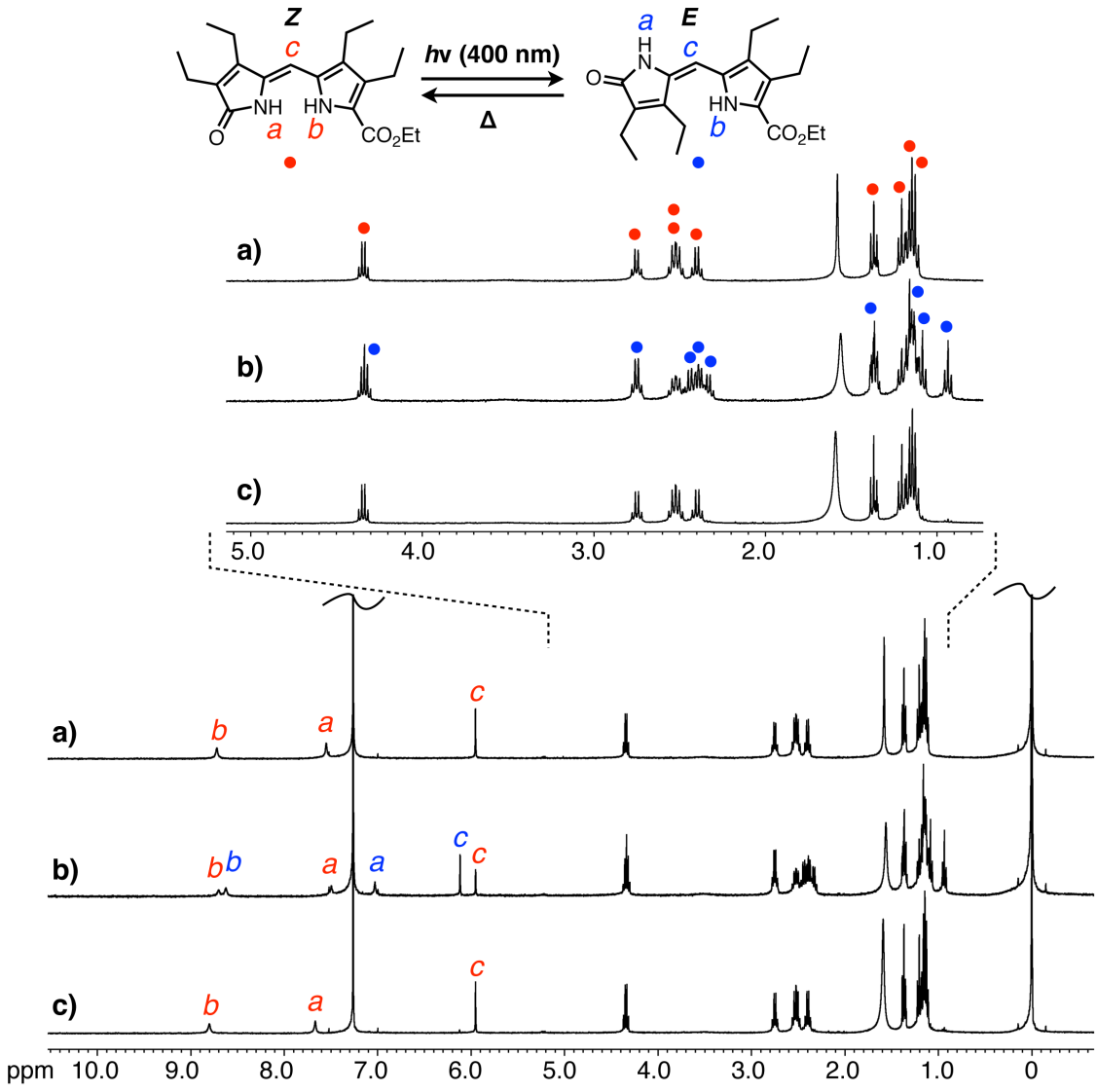


Fig. S6. ^{1}H NMR spectral change of (*Z*)-**7** upon photoirradiation in $CDCl_3$. a) (*Z*)-**7**, b) after 400 nm irradiation for 2 h. c) after standing in the dark for 2 weeks at 25 °C.

Photoisomerization of (*Z*)-1 in $CDCl_3$;

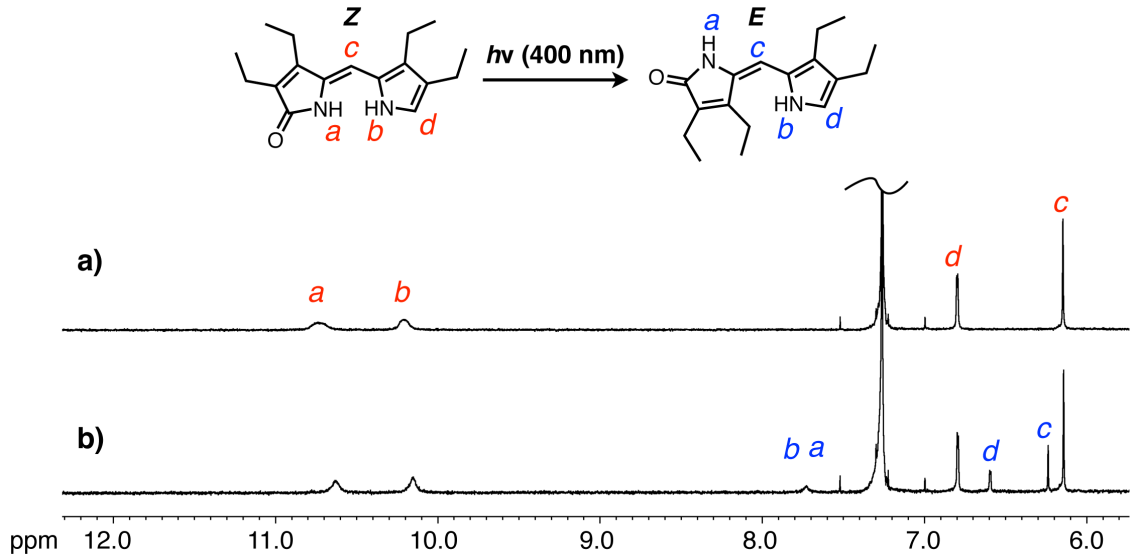


Fig. S7. ^{1}H NMR spectral change of (*Z*)-**1** upon photoirradiation in $CDCl_3$. a) (*Z*)-**1**, b) after 400 nm irradiation for 2h.

Photoisomerization of (*Z*)-2 in $CDCl_3$;

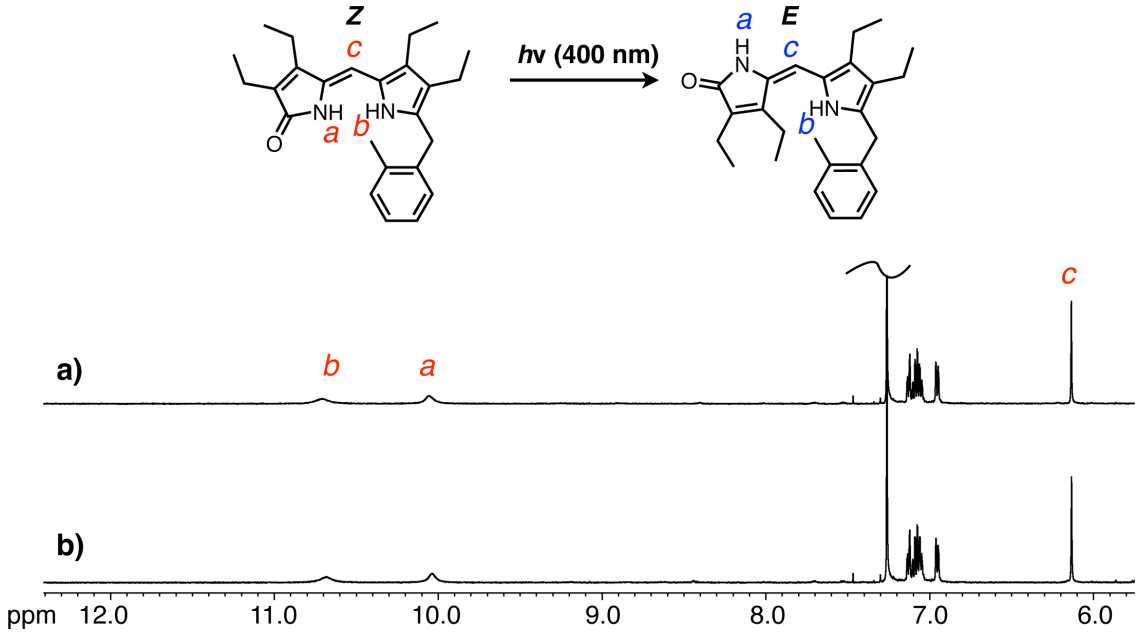


Fig. S8. ^{1}H NMR spectral change of (*Z*)-**2** upon photoirradiation in $CDCl_3$. a) (*Z*)-**2**, b) after 400 nm irradiation for 2 h.

Photoisomerization of (*Z*)-3 in $CDCl_3$;

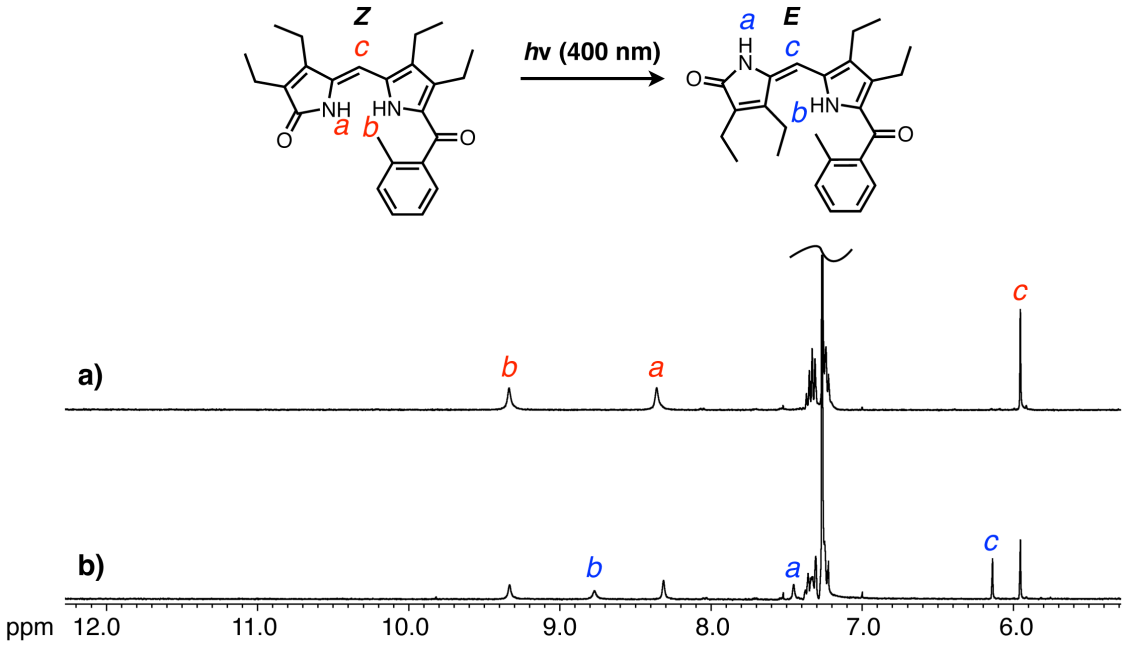


Fig. S9. ^{1}H NMR spectral change of (*Z*)-**3** upon photoirradiation in $CDCl_3$. a) (*Z*)-**3**, b) after 400 nm irradiation for 2 h.

Photoisomerization of (*Z*)-4 in $CDCl_3$;

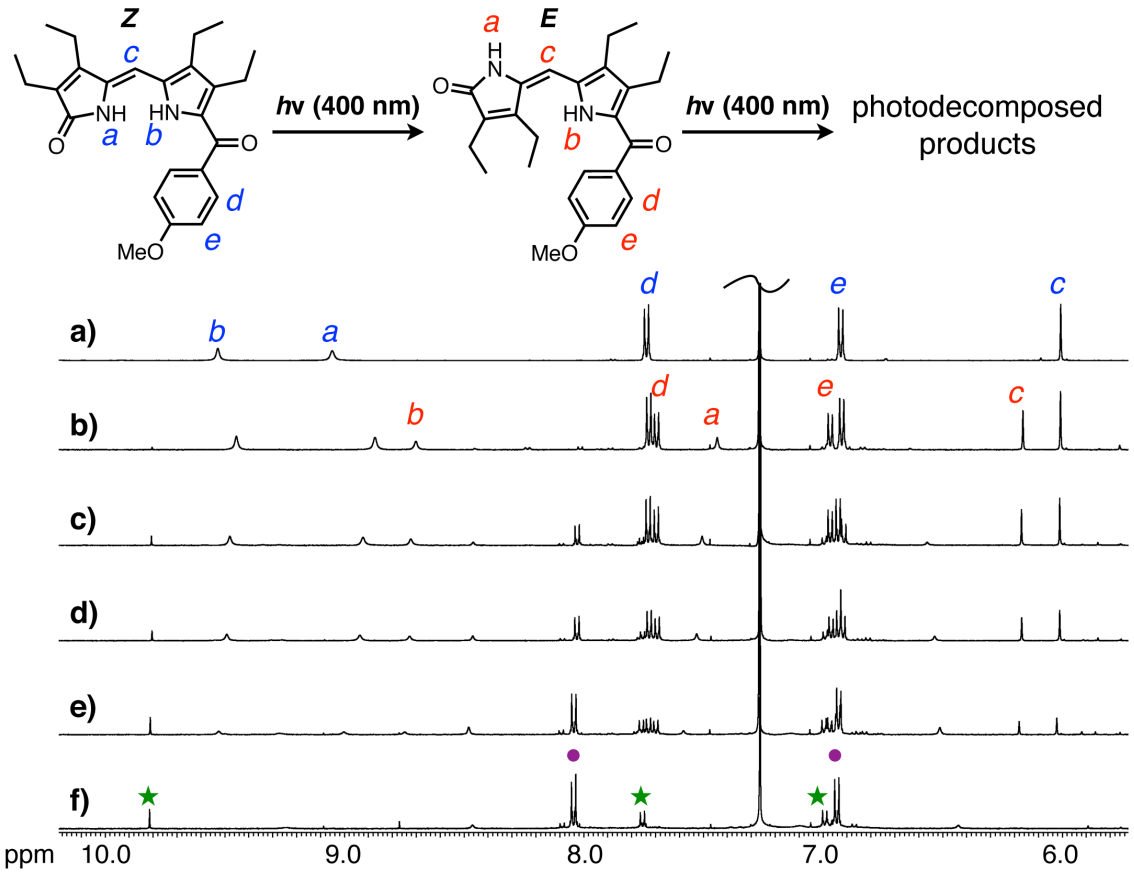


Fig. S10. ^{1}H NMR spectral change of (*Z*)-**4** upon photoirradiation in $CDCl_3$. a) (*Z*)-**4**, b) after 400 nm irradiation for 1 h. Upon prolonged irradiation (c) 2h, d) 3d, e) 5h, f) 8h), only photo-decomposed products were observed. This decomposition was suppressed in a degassed solution.

Photoisomerization of (*Z*)-5 in $CDCl_3$;

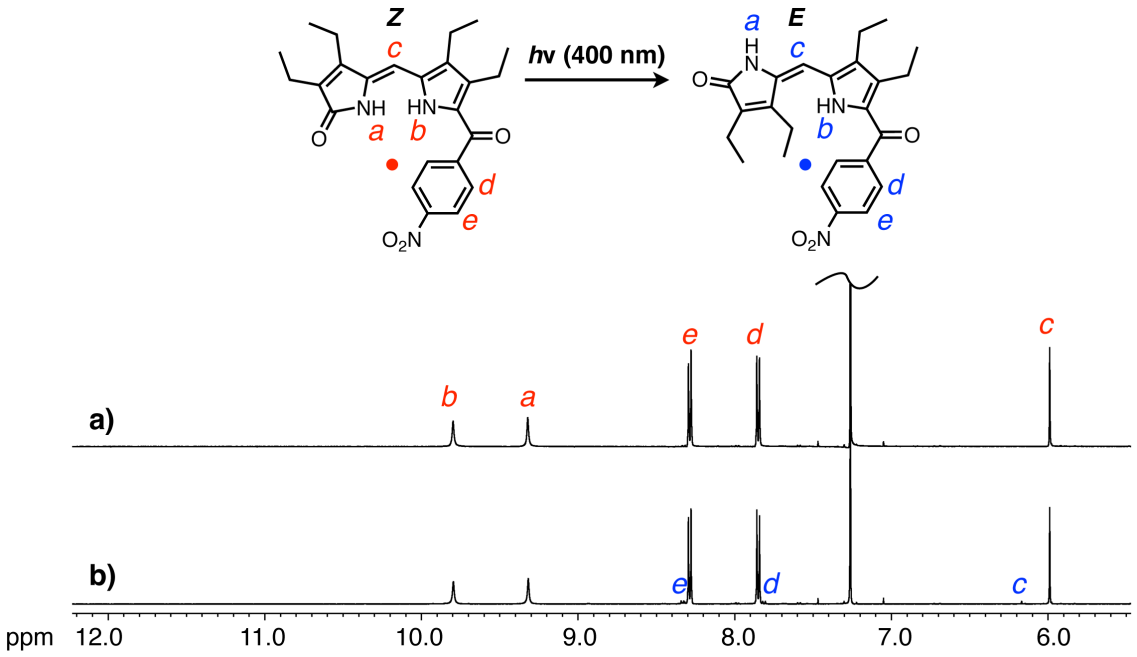


Fig. S11. ^{1}H NMR spectral change of (*Z*)-**5** upon photoirradiation in $CDCl_3$. a) (*Z*)-**5**, b) after 400 nm irradiation for 2 h.

Photoisomerization of (*Z*)-6 in $CDCl_3$;

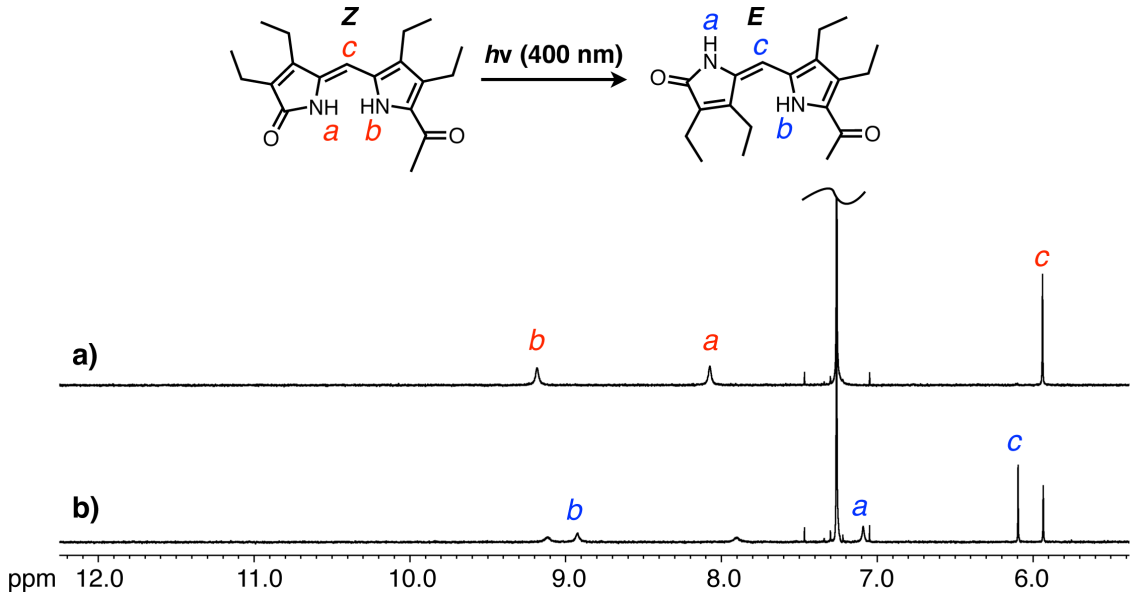


Fig. S12. ^{1}H NMR spectral change of (*Z*)-**6** upon photoirradiation in $CDCl_3$. a) (*Z*)-**6**, b) after 400 nm irradiation for 2 h.

Photoisomerization of (*Z*)-7 in CD_3OD and thermal relaxation at 25 °C;

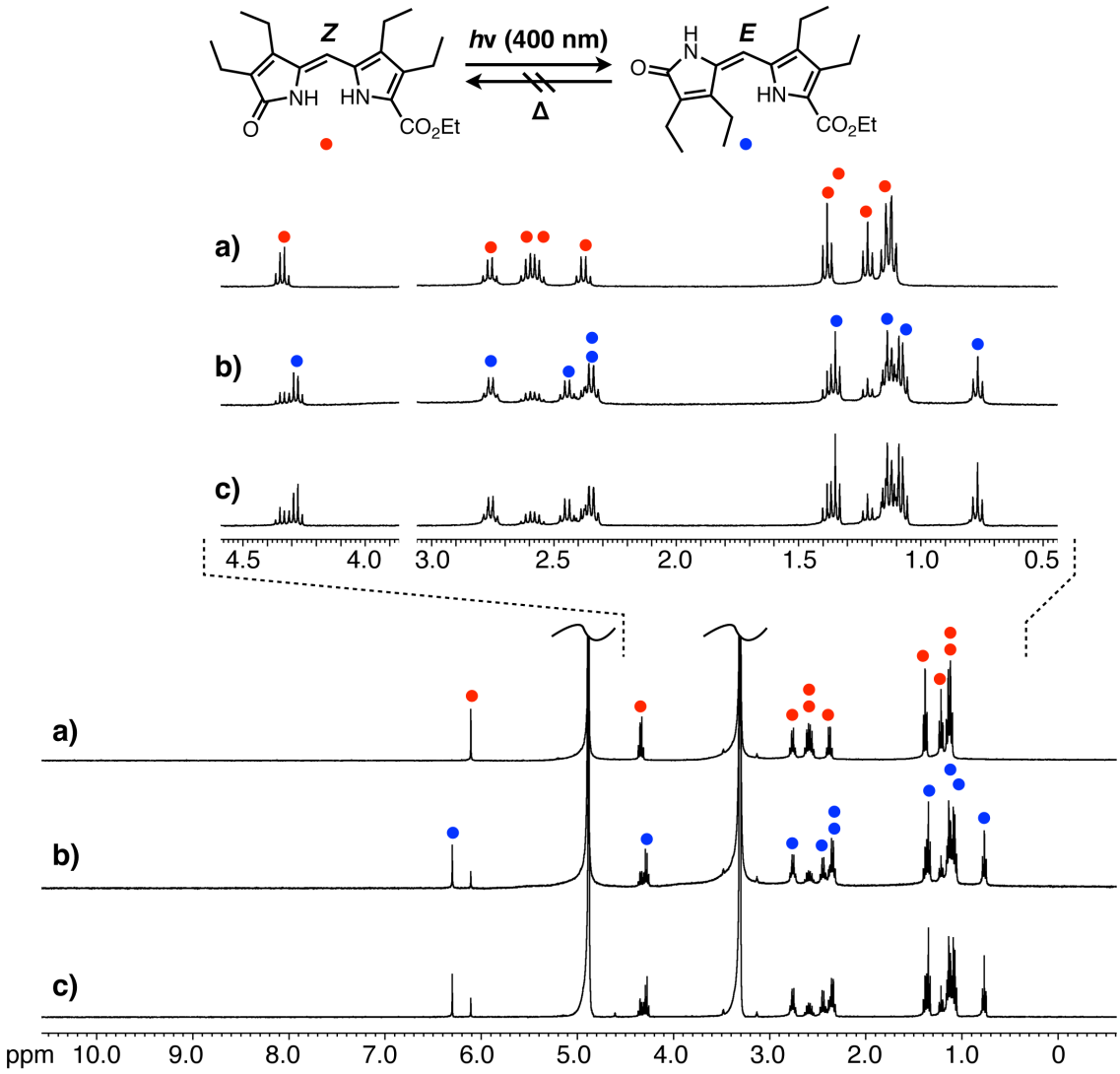


Fig. S13. ^{1}H NMR spectral change of (*Z*)-**7** upon photoirradiation in CD_3OD. a) (*Z*)-**7**, b) after 400 nm irradiation for 2 h, c) after standing in the dark for 2 weeks at 25 °C.

Photoisomerization of (*Z*)-7 in CD_3OD and thermal relaxation at 50 °C;

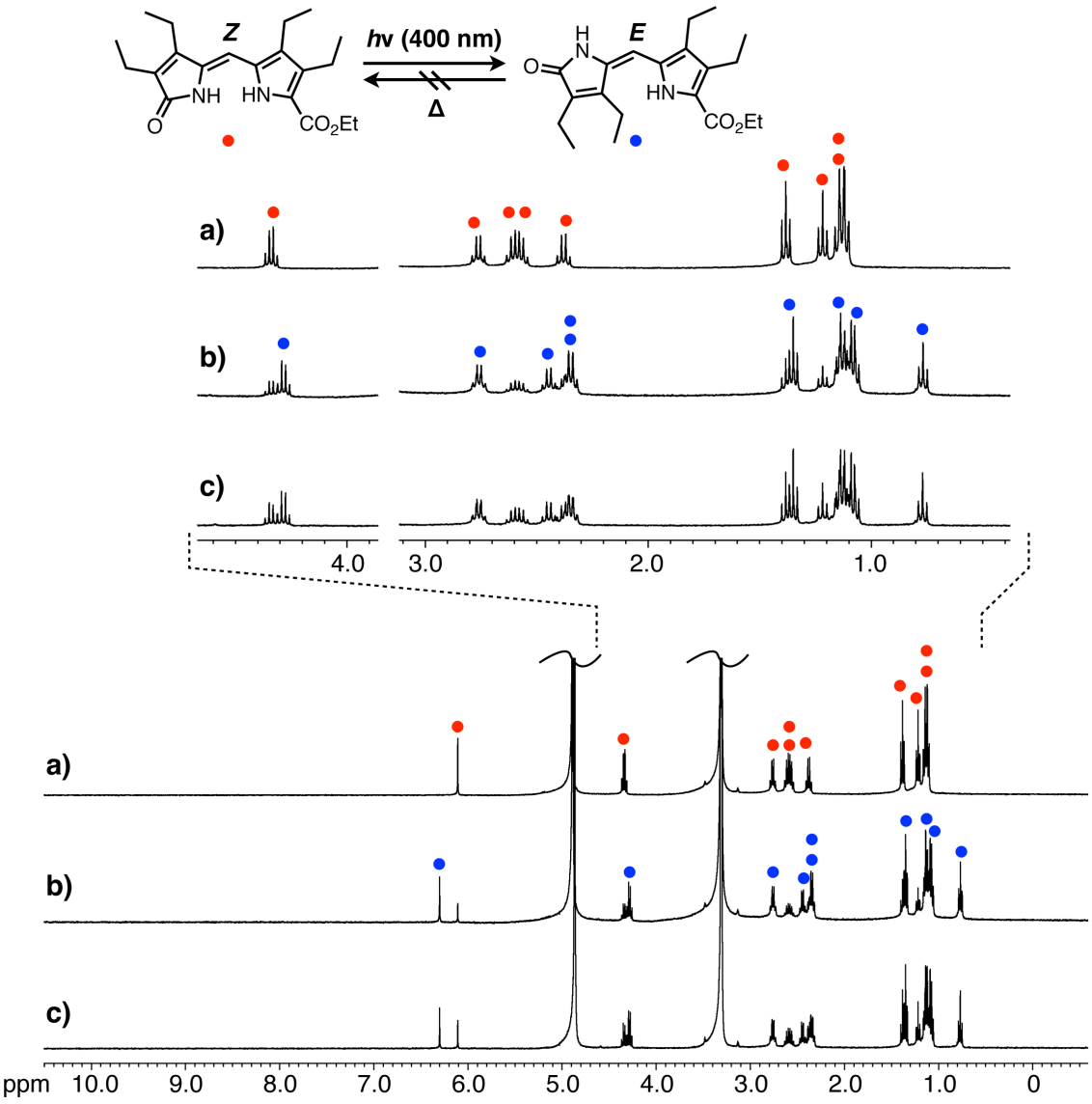


Fig. S14. ^{1}H NMR spectral change of (*Z*)-**7** upon photoirradiation in CD_3OD. a) (*Z*)-**7**, b) after 400 nm irradiation for 2 h, c) after standing in the dark for 100 hr at 50 °C.

Photoisomerization of (*Z*)-7 in DMSO-d_6 and thermal relaxation at 25 °C;

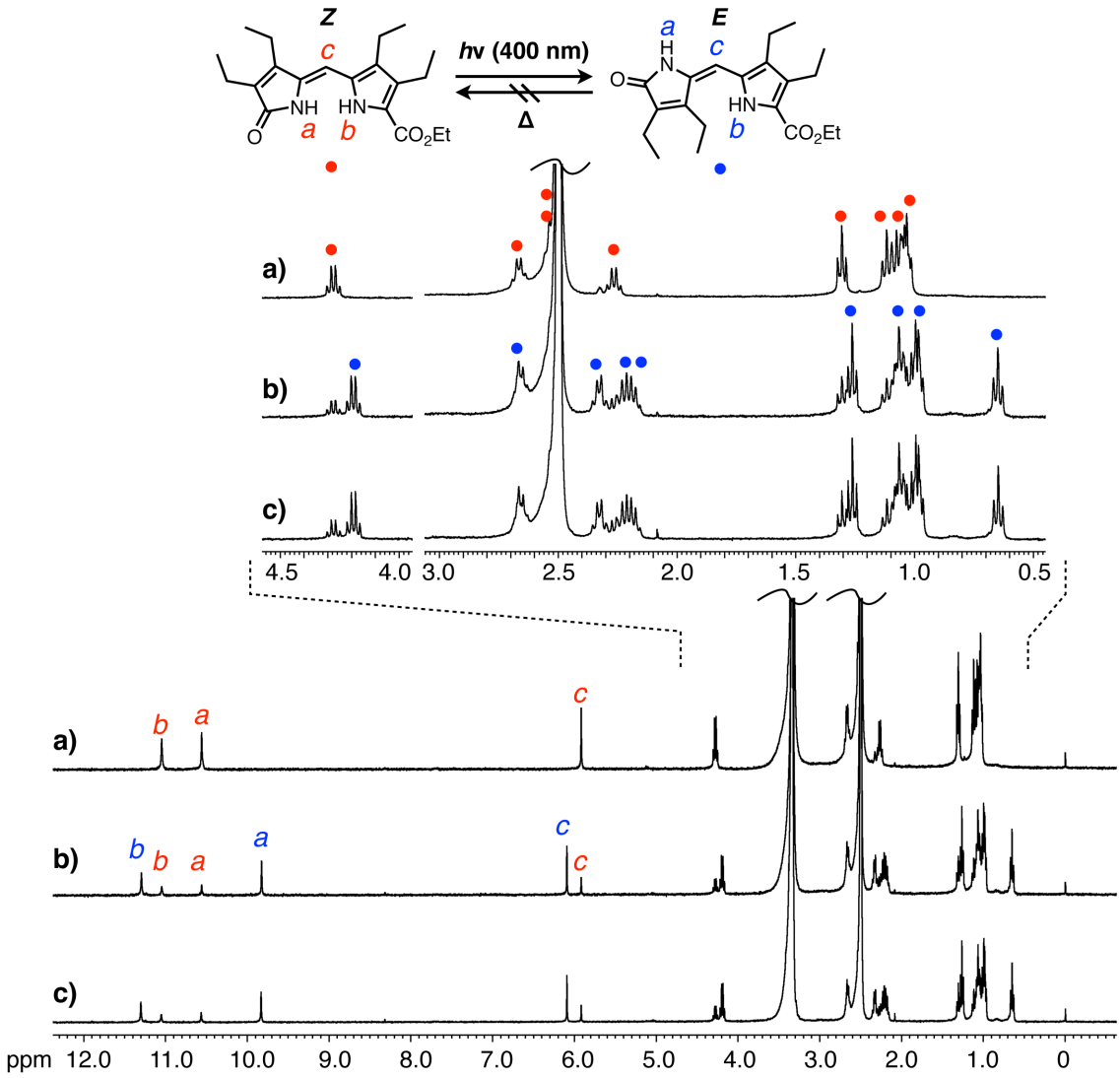


Fig. S15. ^{1}H NMR spectral change of (*Z*)-**7** upon photoirradiation in DMSO-d_6. a) (*Z*)-**7**, b) after 400 nm irradiation for 2 h, c) after being left at 25 °C for 2 weeks.

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