Supporting Information Materials

for

2,2′-Disilylazobenzenes Featuring Intramolecular Double Nitrogen···Silicon Coordination: A Photoisomerizable Fluorophore

Naokazu Kano,* Masaki Yamamura and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Contents

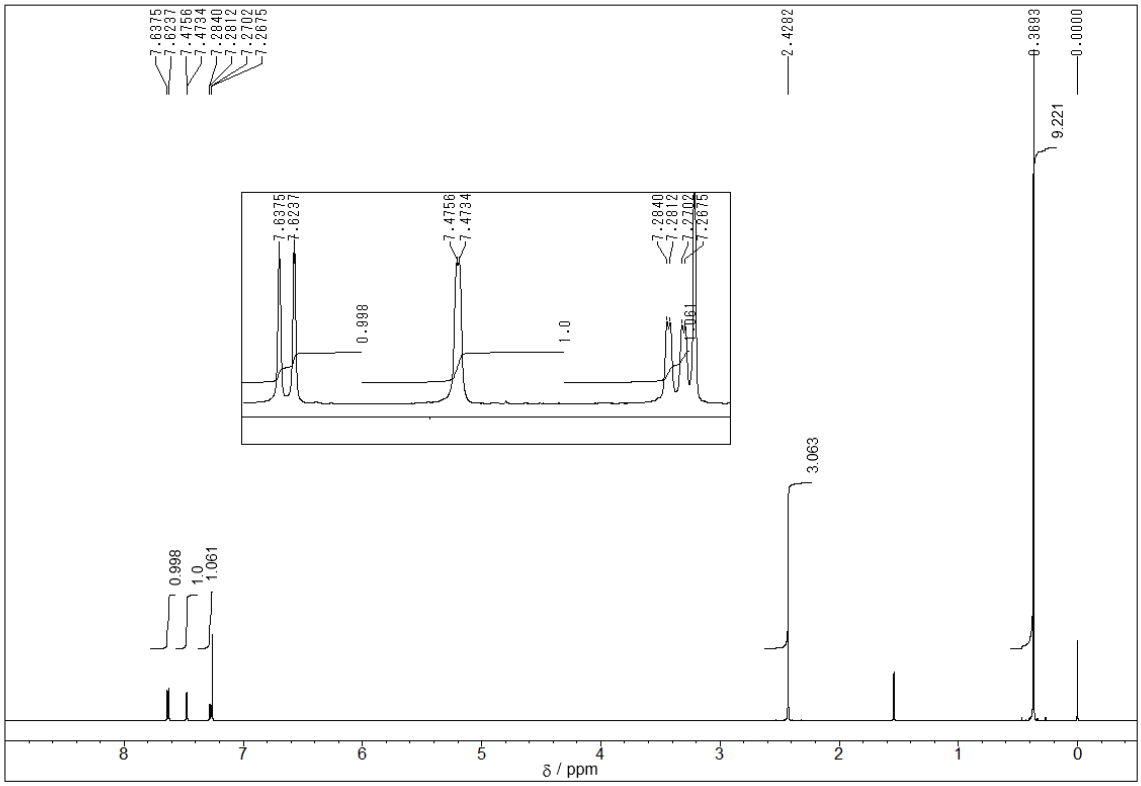

Figure S1. ^{1}H NMR spectrum of (*E*)-**4a** in $CDCl_3$ (600 MHz).

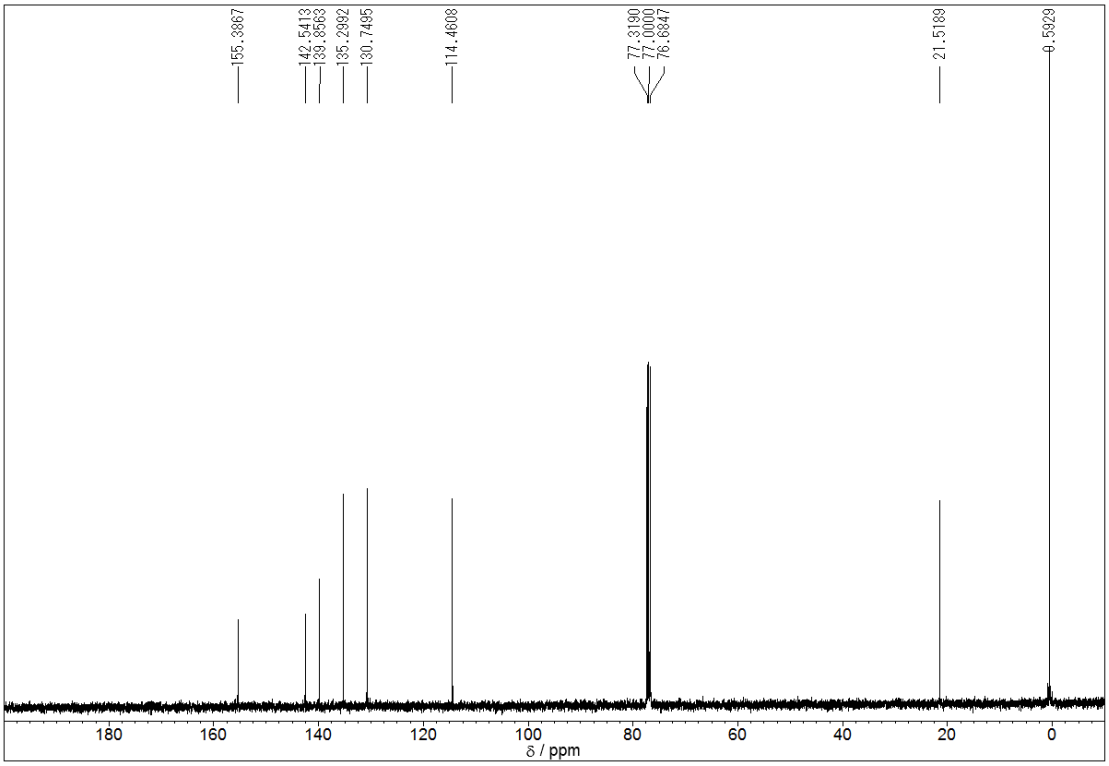

Figure S2. ^{13}C NMR spectrum of (*E*)-**4a** in $CDCl_3$ (100 MHz).

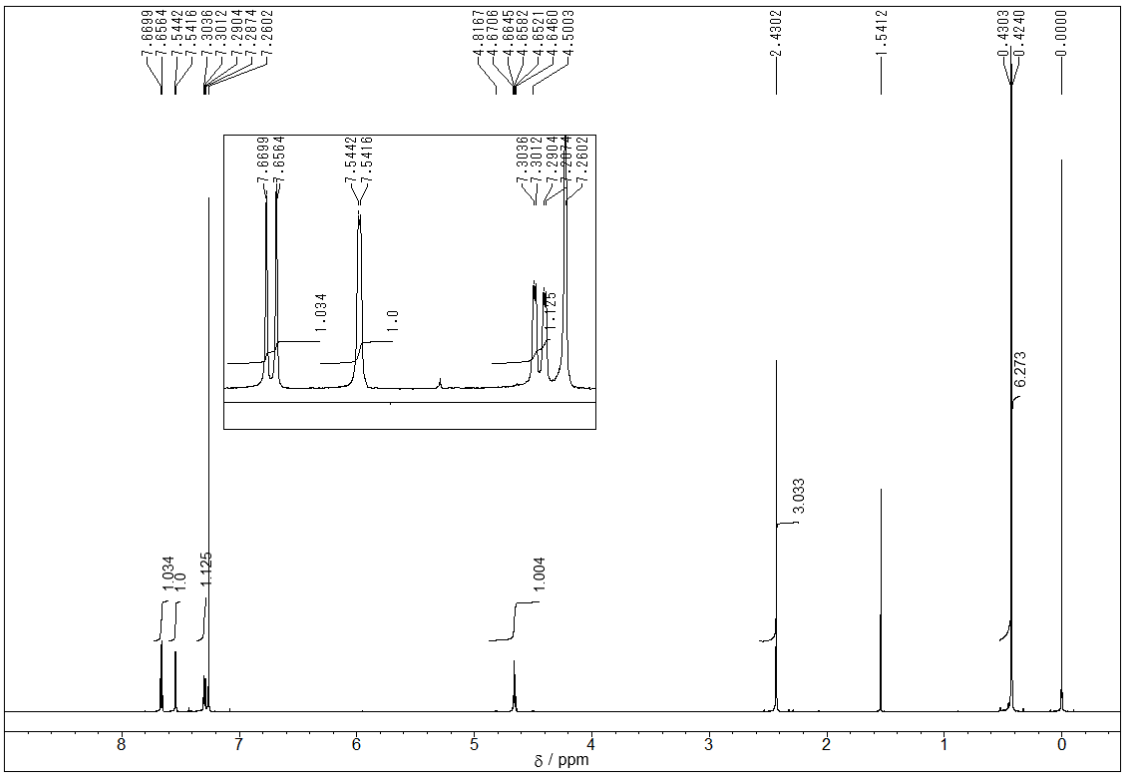

Figure S3. ^{1}H NMR spectrum of (*E*)-**4b** in $CDCl_3$ (600 MHz).

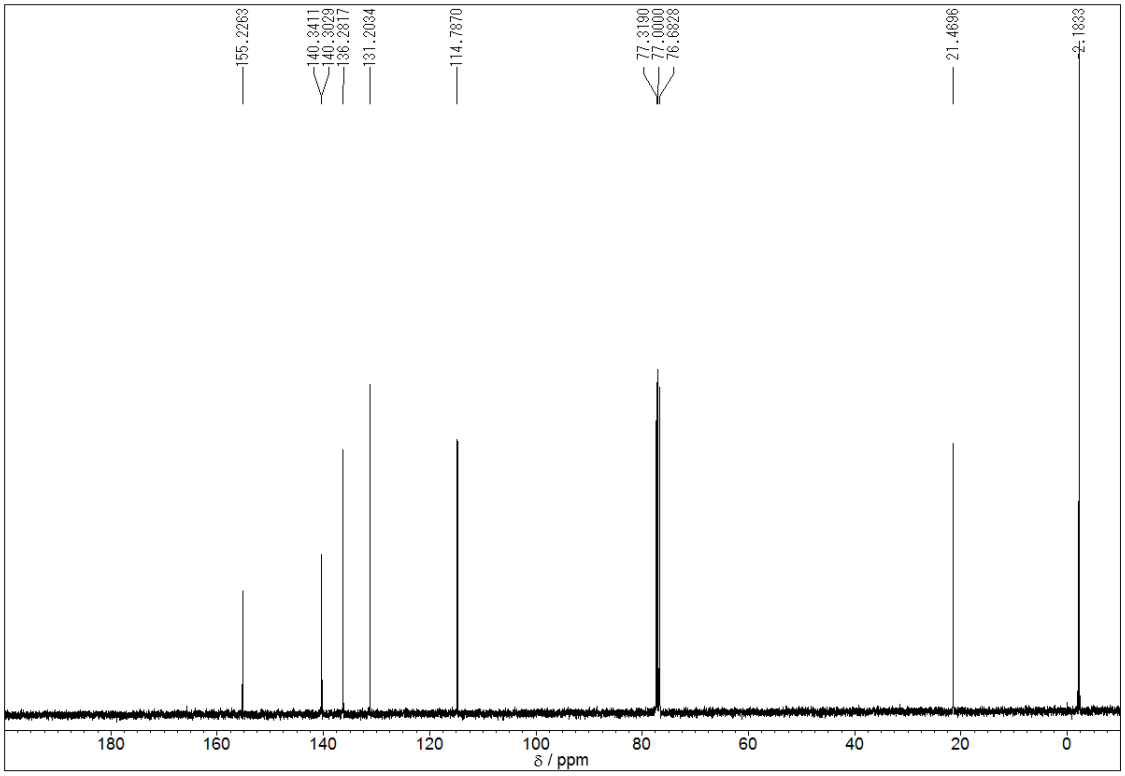

Figure S4. ^{13}C NMR spectrum of (*E*)-**4b** in $CDCl_3$ (100 MHz).

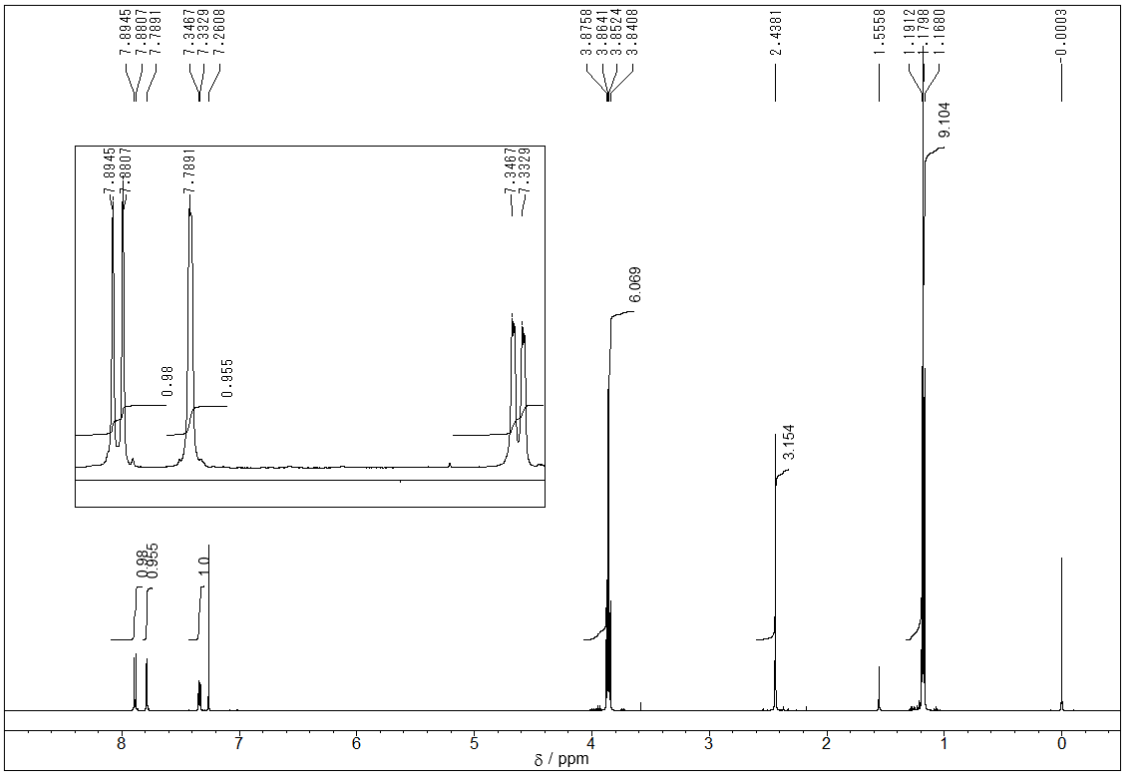

Figure S5. ^{1}H NMR spectrum of (*E*)-**4c** in $CDCl_3$ (600 MHz).

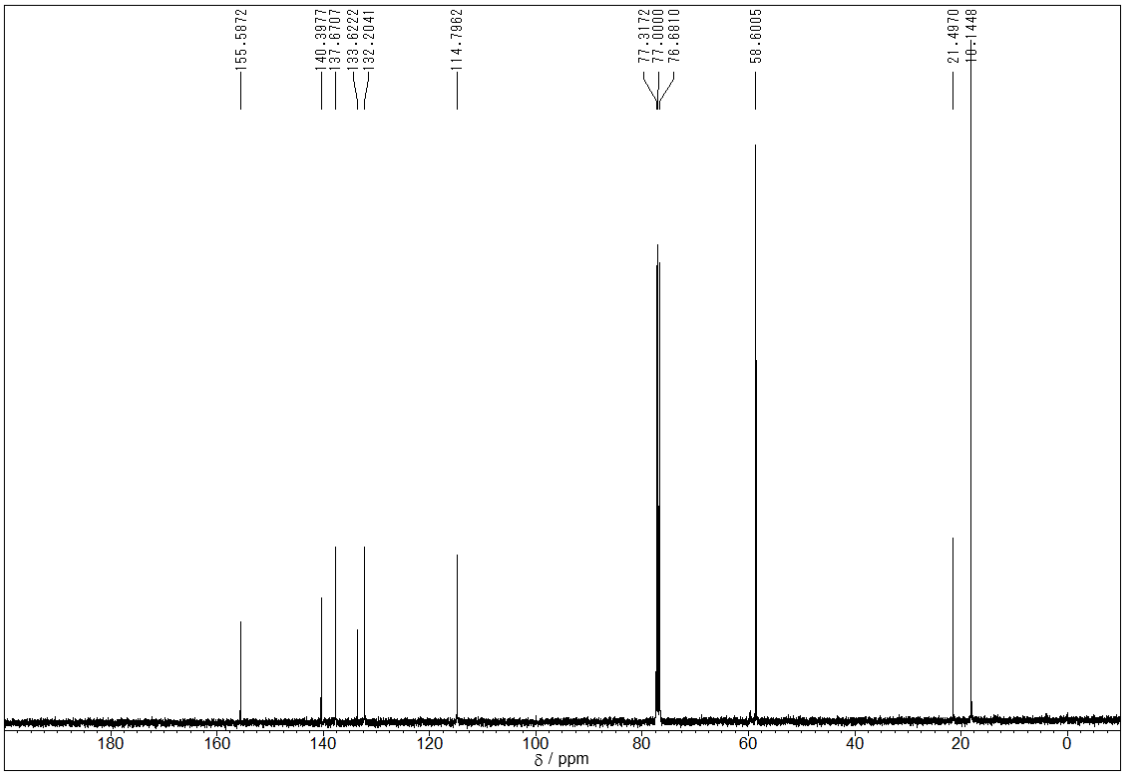

Figure S6. ^{13}C NMR spectrum of (*E*)-**4c** in $CDCl_3$ (100 MHz).

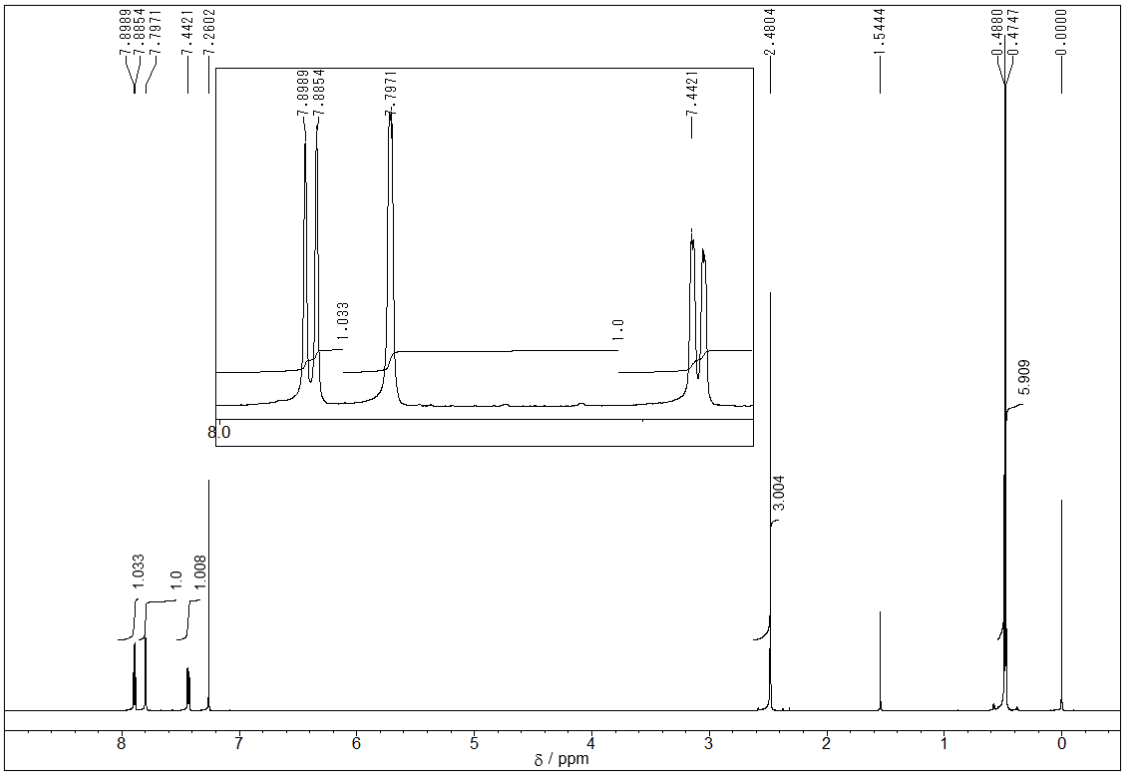

Figure S7. ^{1}H NMR spectrum of (*E*)-**4d** in $CDCl_3$ (600 MHz).

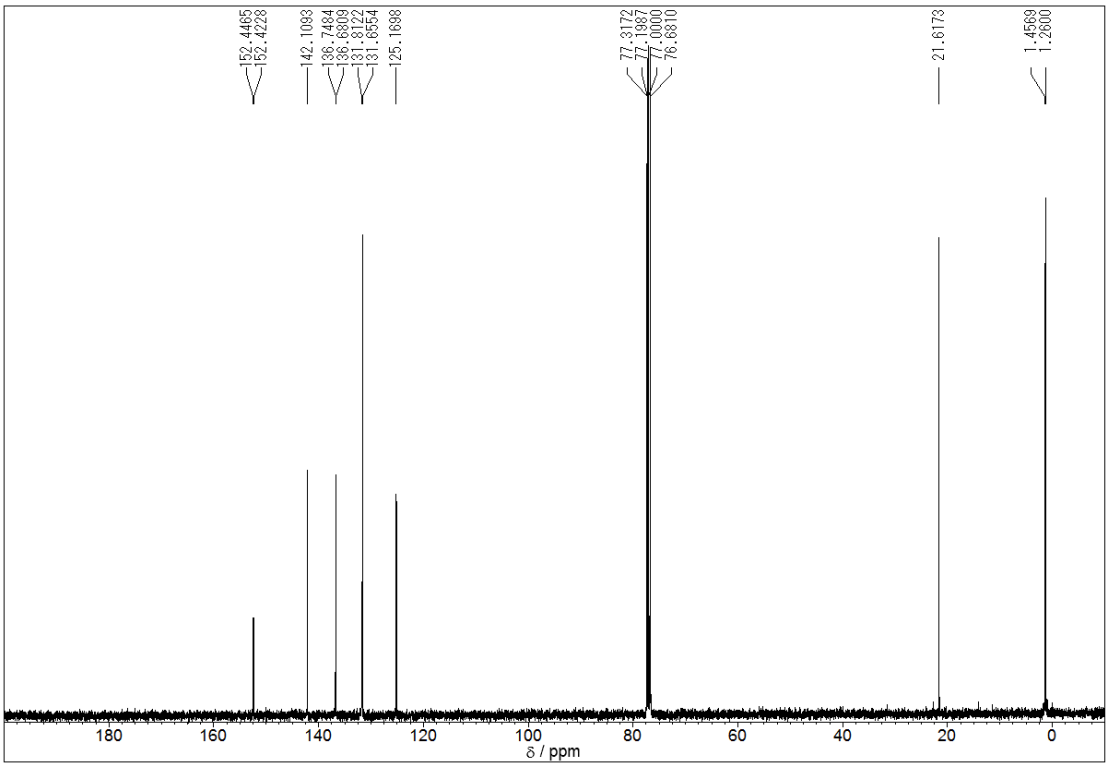

Figure S8. ^{13}C NMR spectrum of (*E*)-**4d** in $CDCl_3$ (100 MHz).

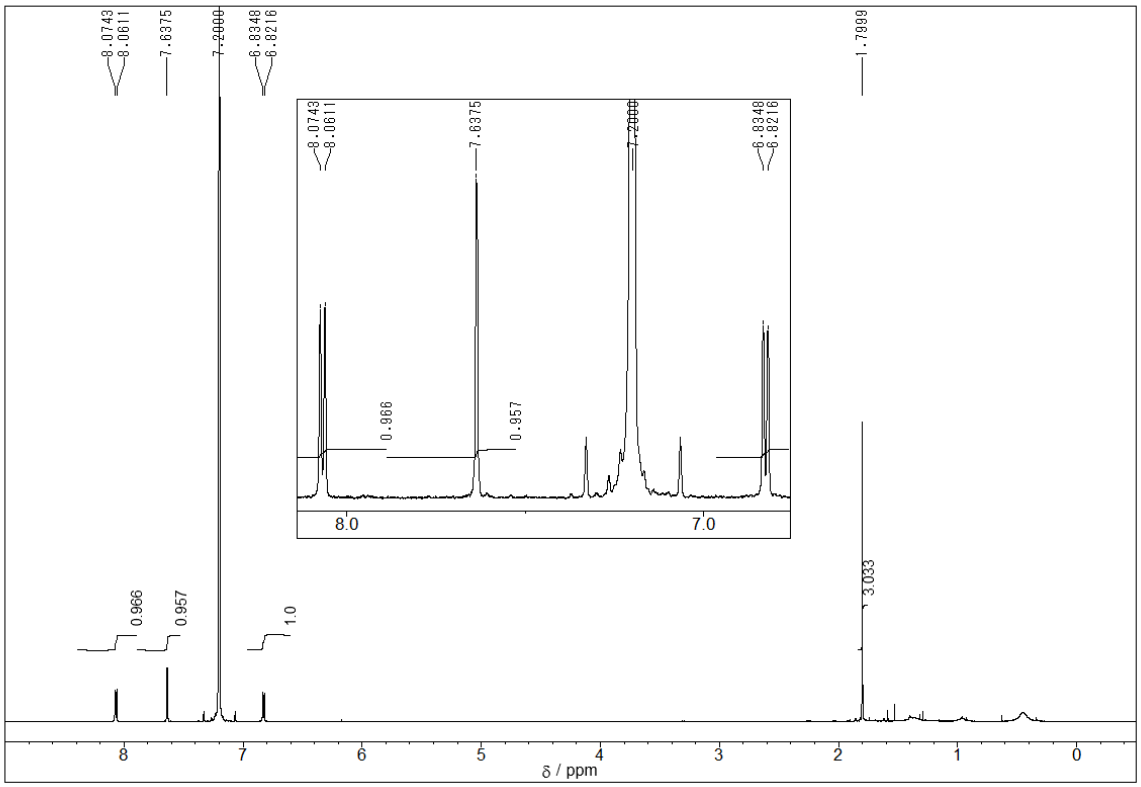

Figure S9. ^{1}H NMR spectrum of (*E*)-**4e** in C_6D_6 (600 MHz).

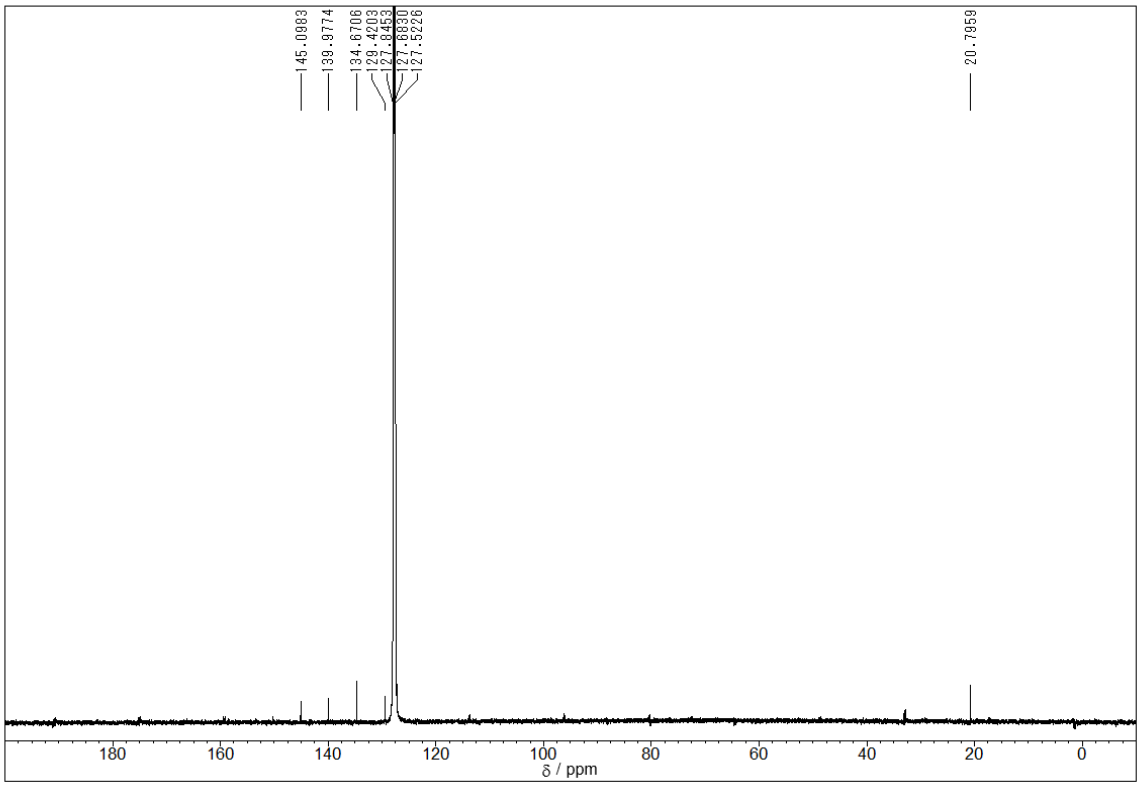

Figure S10. ^{13}C NMR spectrum of (*E*)-**4e** in C_6D_6 (150 MHz).

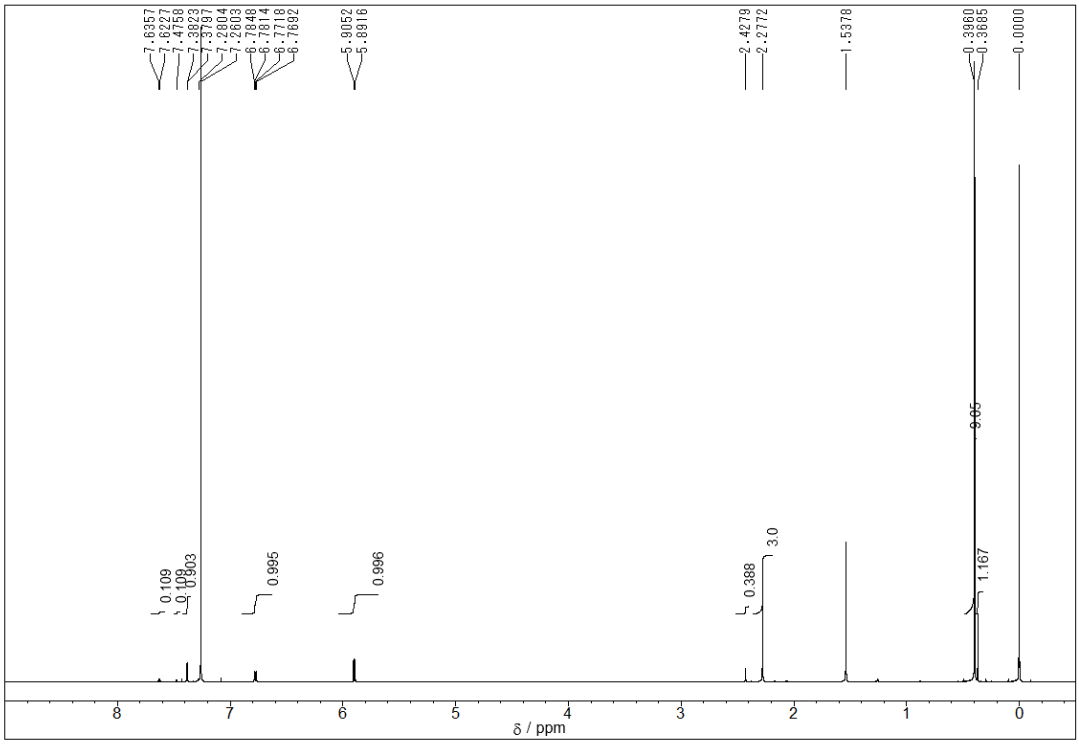

Figure S11. ^{1}H NMR spectrum of a mixture of (*E*)- and (*Z*)-**4a** in 11/89 ratio in $CDCl_3$ after photoisomerization.

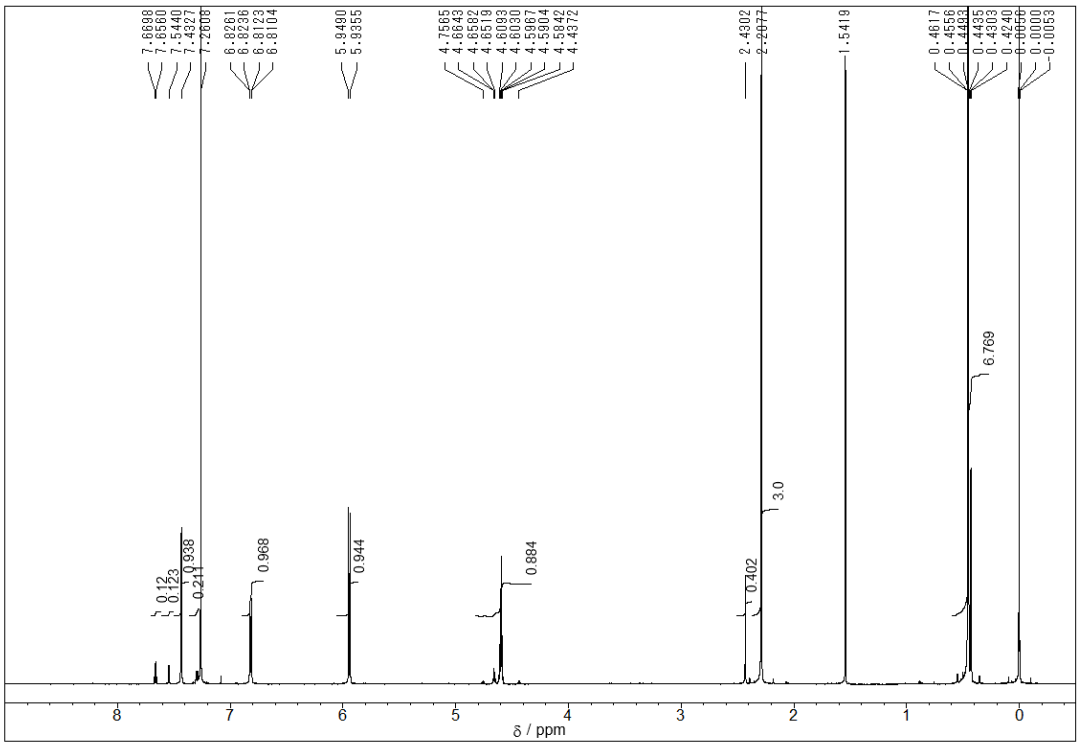

Figure S12. ^{1}H NMR spectrum of a mixture of (*E*)- and (*Z*)-**4b** in 12/88 ratio in $CDCl_3$ after photoisomerization.

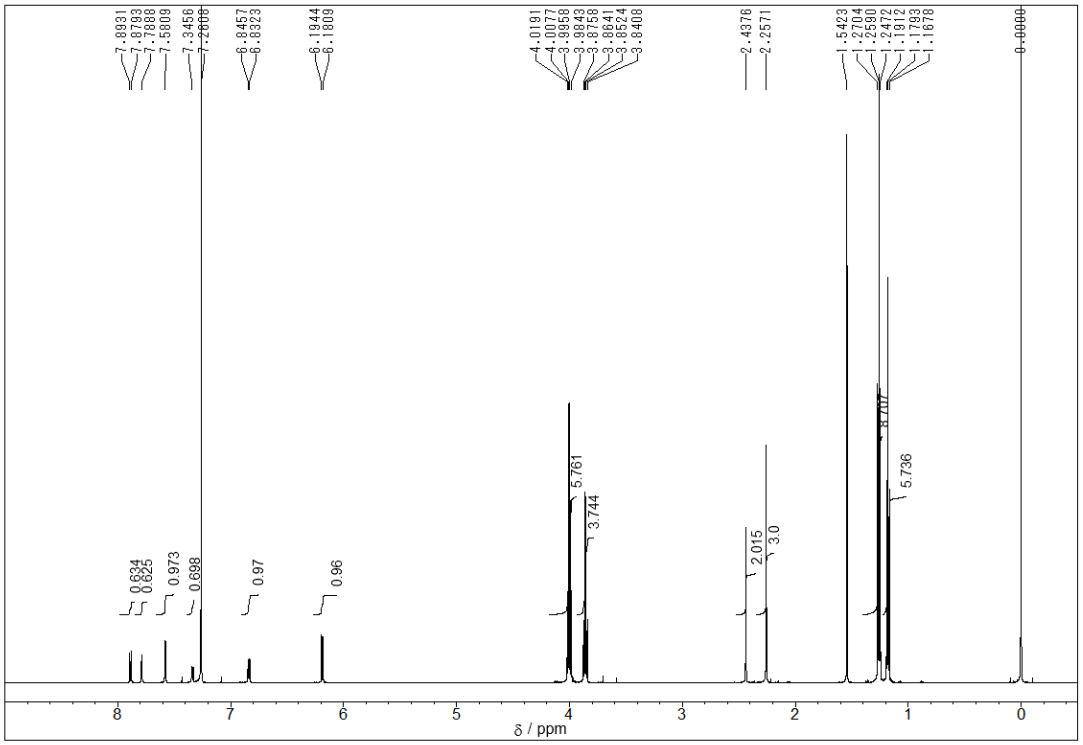

Figure S13. ^{1}H NMR spectrum of a mixture of (*E*)- and (*Z*)-**4c** in 40/60 ratio in $CDCl_3$ after photoisomerization.

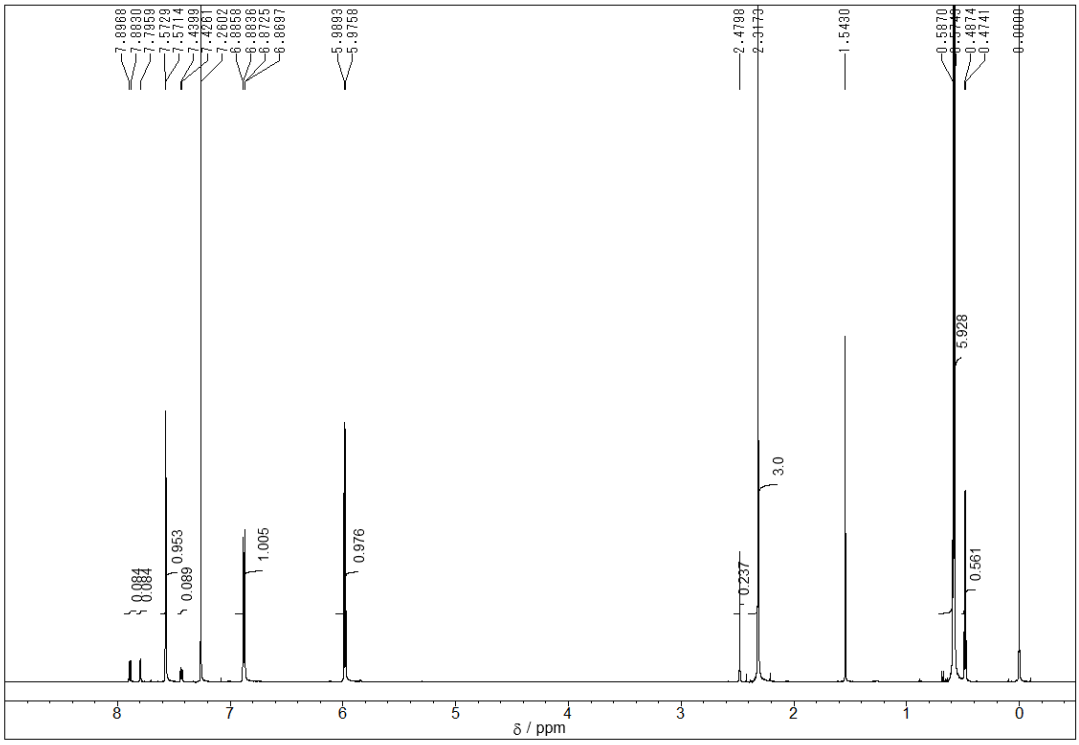

Figure S14. ^{1}H NMR spectrum of a mixture of (*E*)- and (*Z*)-**4d** in 7/93 ratio in $CDCl_3$ after photoisomerization.

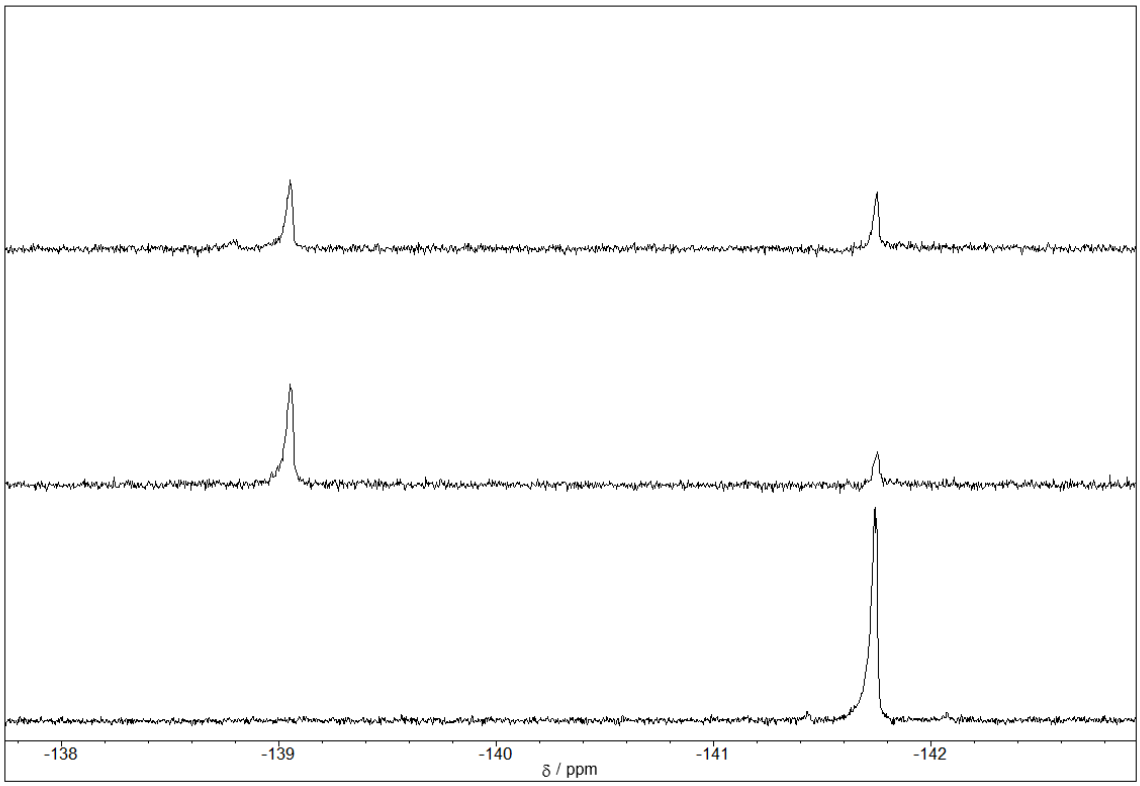

Figure S15. ^{19}F NMR spectrum of a mixture of (*E*)- and (*Z*)-**4e** in hexane (C_6D_6) after photoisomerization. Bottom: initial state (only (*E*)-**4e**), middle: photostationary state at 365 nm (a mixture of (*E*)- and (*Z*)-**4e** in 21/79 ratio), and top: photostationary state at 436 nm (a mixture of (*E*)- and (*Z*)-**4e** in 40/60 ratio).

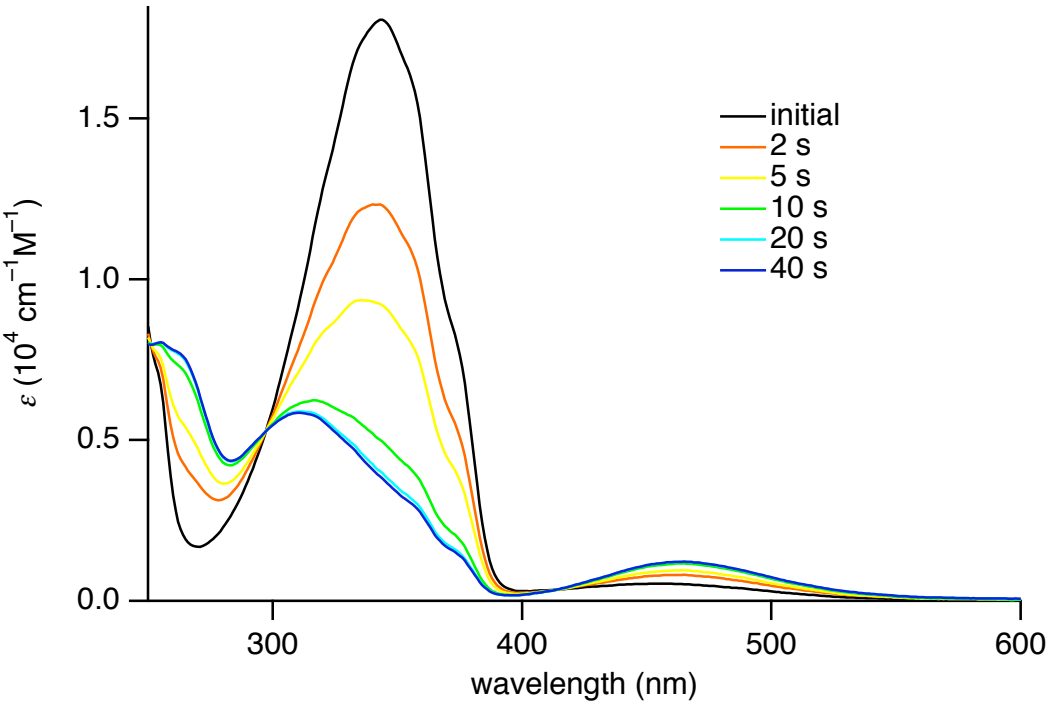

Figure S16. UV-vis absorption spectral change of (*E*)-**4a** upon photoirradiation (hexane, Hg-lamp, 400 W, 365 nm).

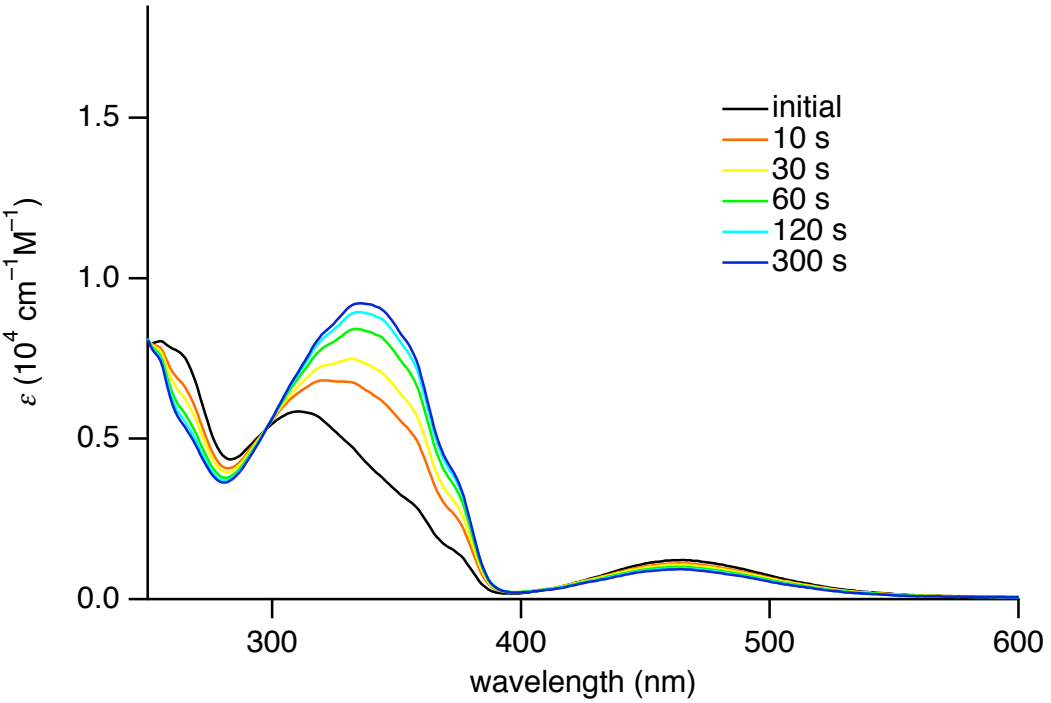

Figure S17. UV-vis absorption spectral change of (*Z*)-**4a** (PPS at 365 nm) upon photoirradiation (hexane, Hg-lamp, 400 W, 436 nm).

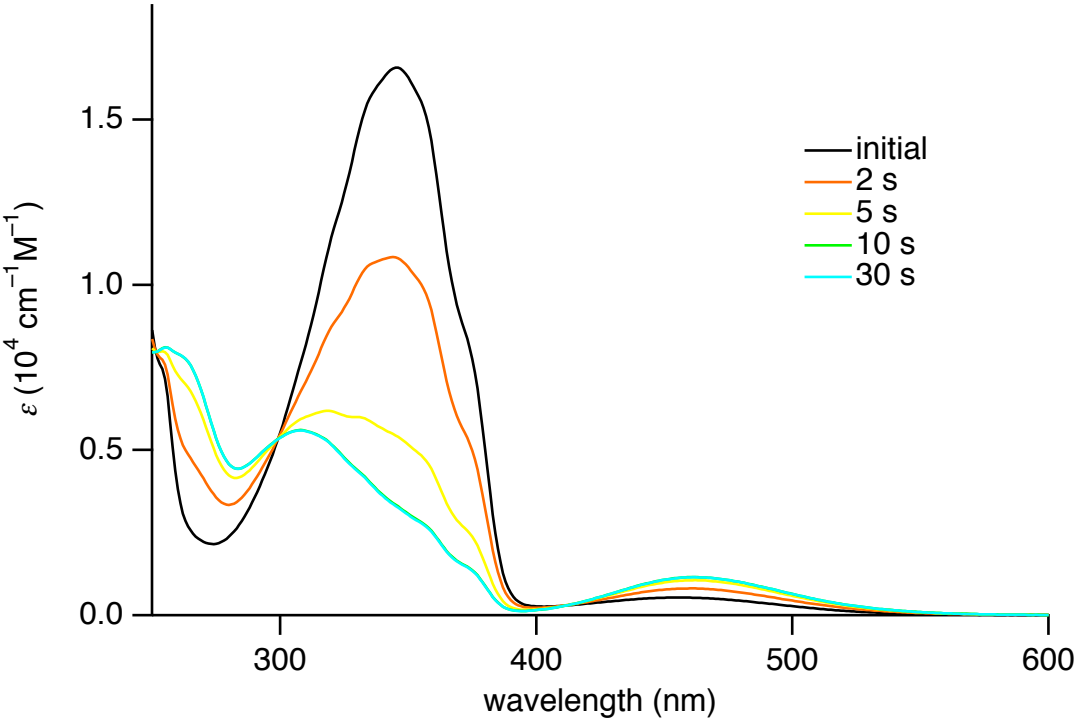

Figure S18. UV-vis absorption spectral change of (*E*)-**4b** upon photoirradiation (hexane, Hg-lamp, 400 W, 365 nm).

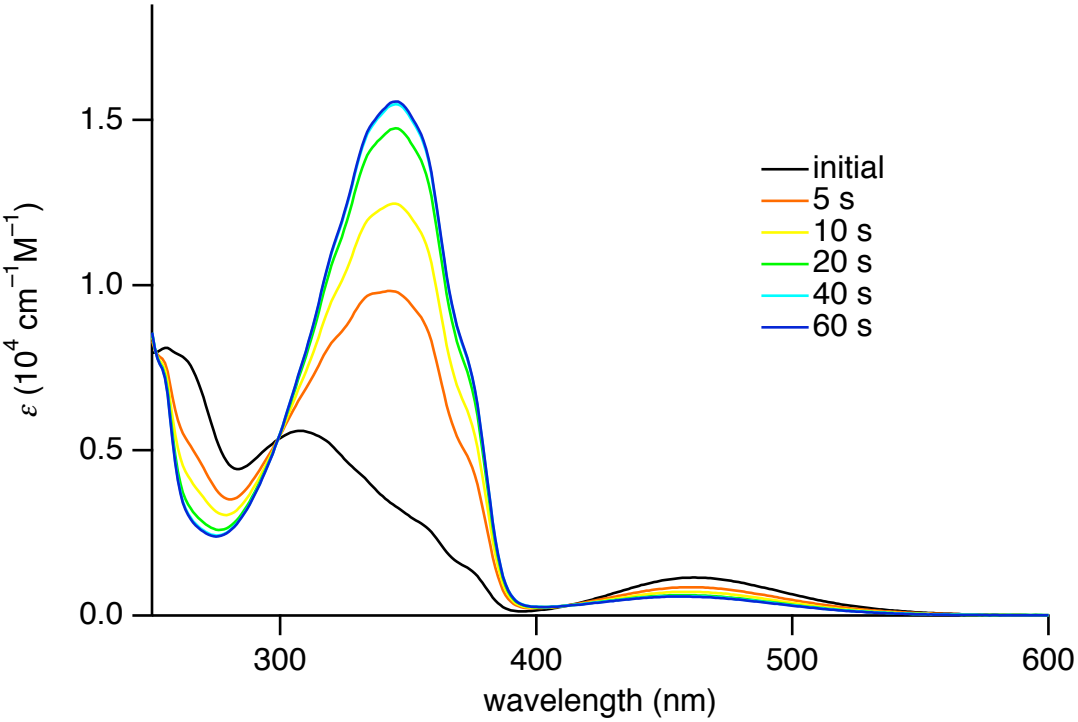

Figure S19. UV-vis absorption spectral change of (*Z*)-**4b** (PPS at 365 nm) upon photoirradiation (hexane, Hg-lamp, 400 W, 436 nm).

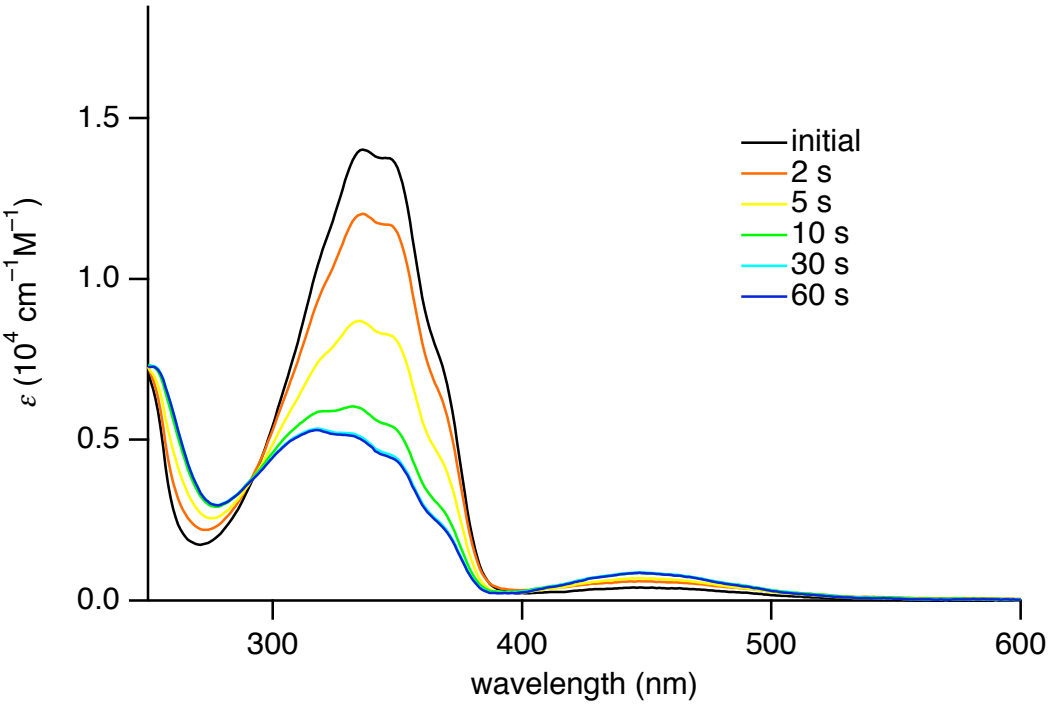

Figure S20. UV-vis absorption spectral change of (*E*)-**4c** upon photoirradiation (hexane, Hg-lamp, 400 W, 365 nm).

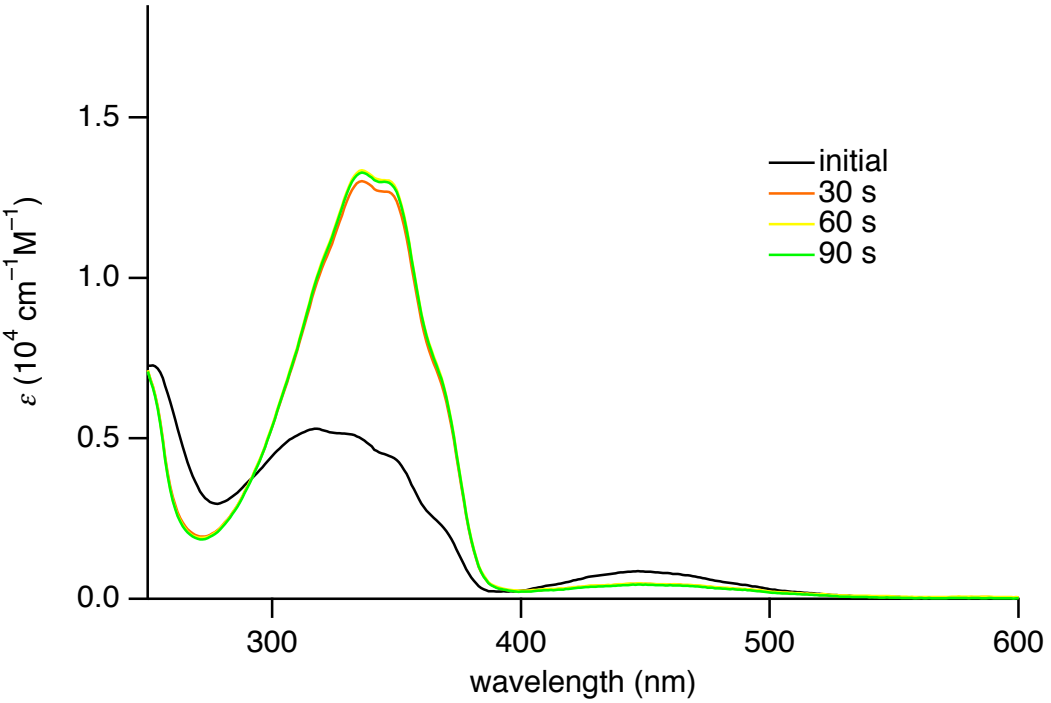

Figure S21. UV-vis absorption spectral change of (*Z*)-**4c** (PPS at 365 nm) upon photoirradiation (hexane, Hg-lamp, 400 W, 436 nm).

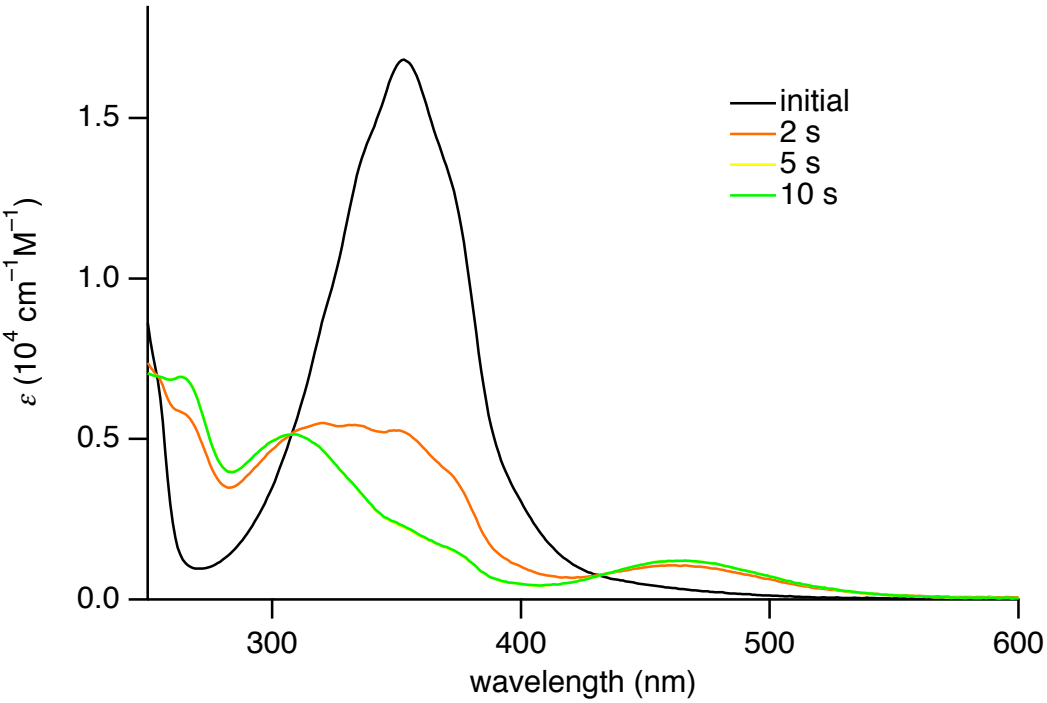

Figure S22. UV-vis absorption spectral change of (*E*)-**4d** upon photoirradiation (hexane, Hg-lamp, 400 W, 365 nm).

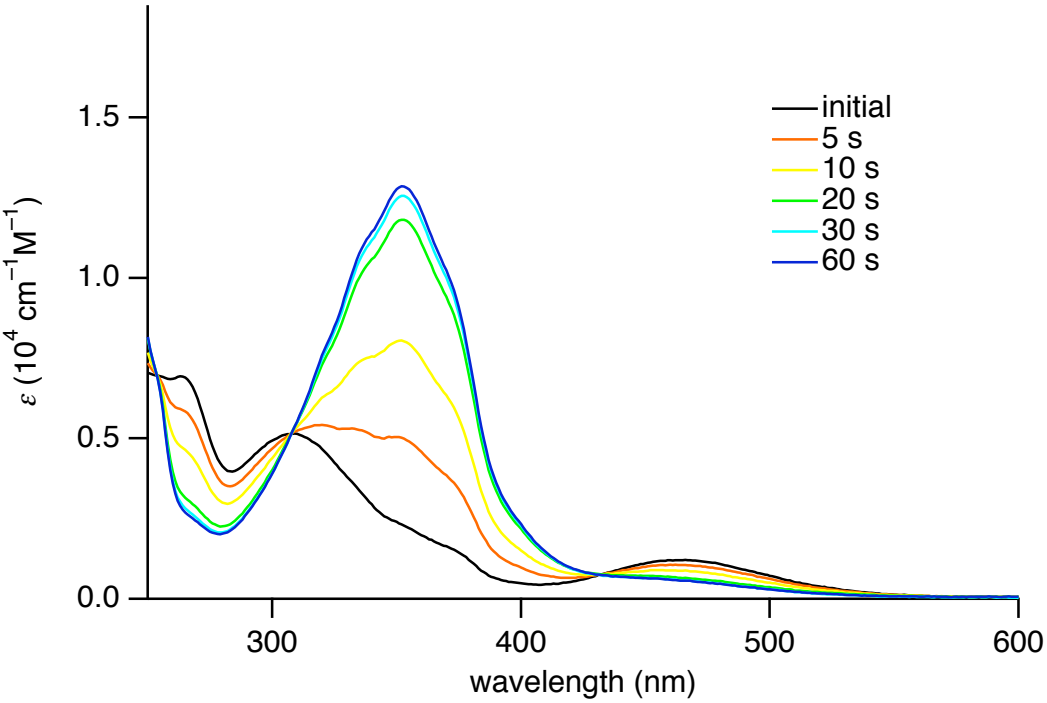

Figure S23. UV-vis absorption spectral change of (*Z*)-**4d** (PPS at 365 nm) upon photoirradiation (hexane, Hg-lamp, 400 W, 436 nm).

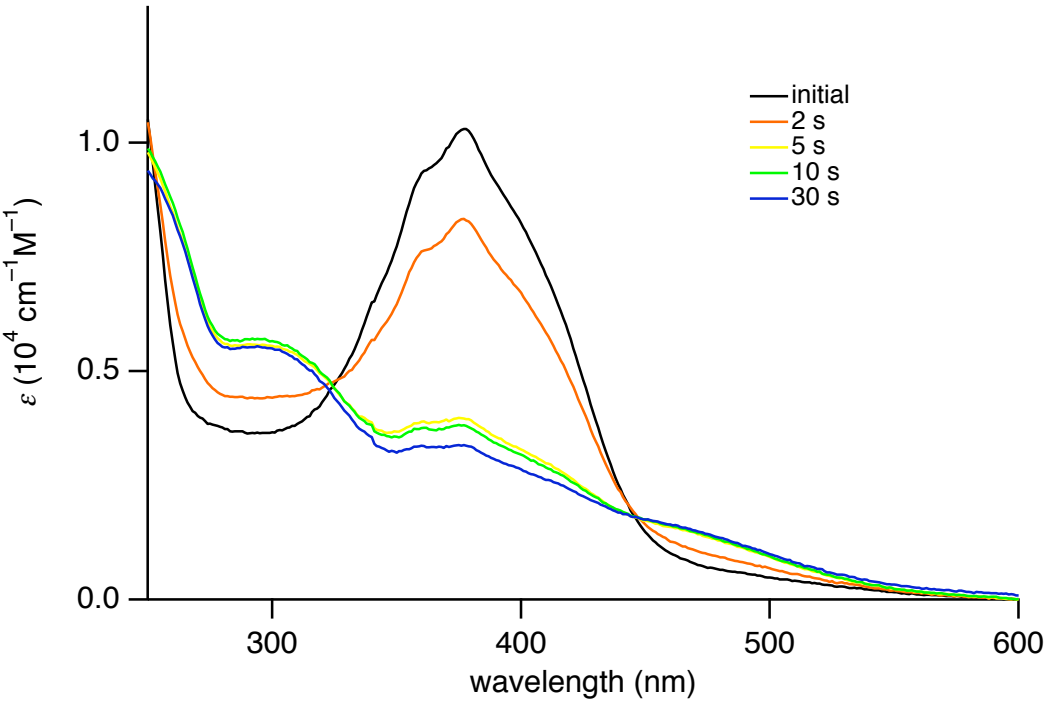

Figure S24. UV-vis absorption spectral change of (*E*)-**4e** upon photoirradiation (hexane, Hg-lamp, 400 W, 365 nm).

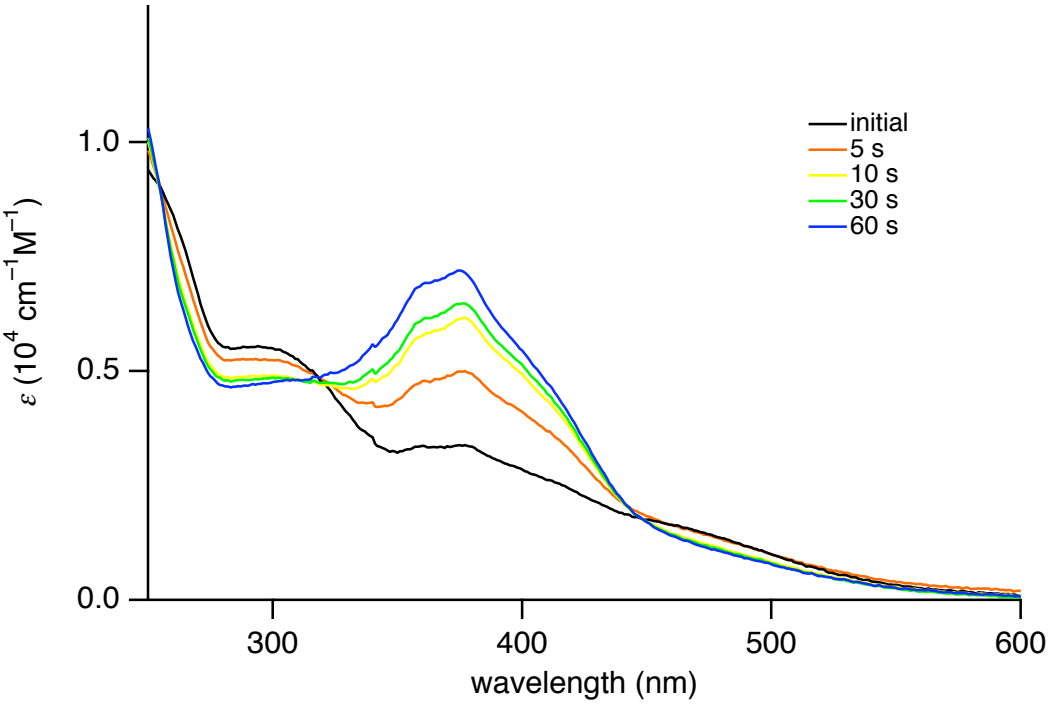

Figure S25. UV-vis absorption spectral change of (*Z*)-**4e** (PPS at 365 nm) upon photoirradiation (hexane, Hg-lamp, 400 W, 436 nm).

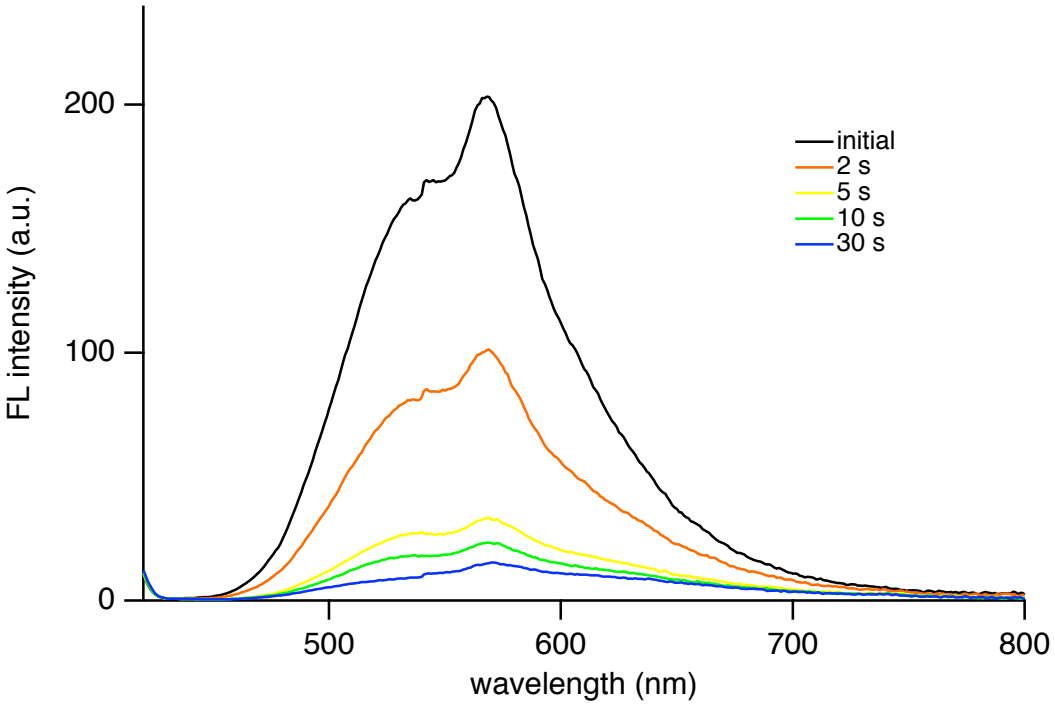

Figure S26. Fluorescence spectral change of (*E*)-**4e** upon photoirradiation (hexane, λ_{ex} = 380 nm, Hg-lamp, 400 W, 365 nm).

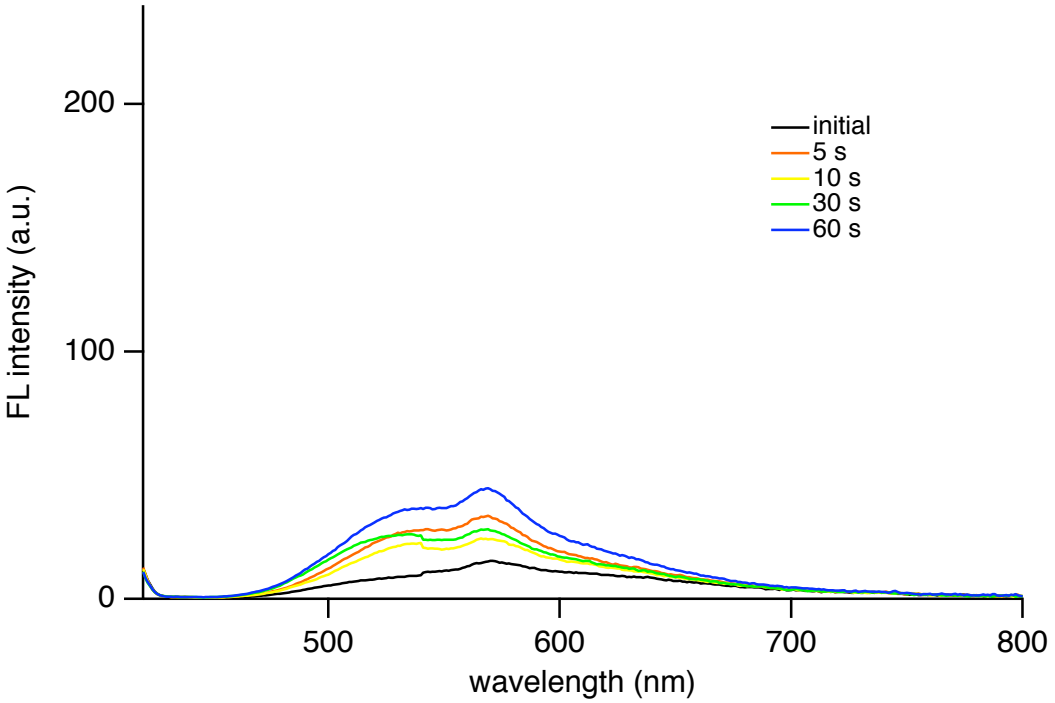

Figure S27. Fluorescence spectral change of (*Z*)-**4e** (PPS at 365 nm) upon photoirradiation (hexane, λ_{ex} = 380 nm, Hg-lamp, 400 W, 436 nm).

(A) (B) (C)

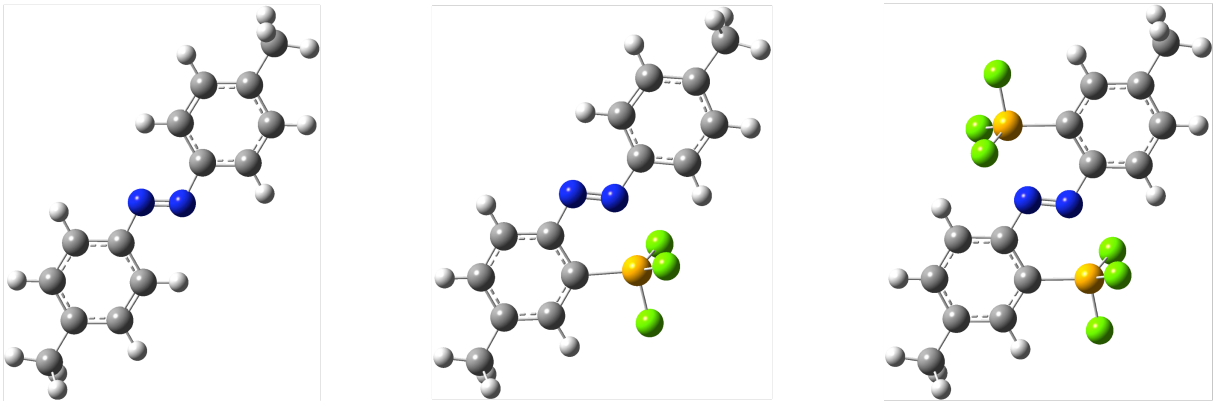

Figure S28. Optimized structures of (A) (*E*)-**5**, (B) (*E*)-**6**, and (C) (*E*)-**4e**. (Magenta: silicon; gray: carbon; yellow-green: fluorine; white: hydrogen; blue: nitrogen).

Table S1. Singlet excited energies of (*E*)-**5**, (*E*)-**6**, and (*E*)-**4e** calculated at the B3PW91/6-311++G(2d,p) level.

		transition (assignment is in parentheses)	excitation energy / eV (oscillator strength, *f*)
(*E*)-**5**	S_1	HOMO–1 → LUMO (n,π*)	2.60 (0.0000)
	S_2	HOMO → LUMO (π,π*)	3.54 (0.9510)
(*E*)-**6**	S_1	HOMO–1 → LUMO (n,π*)	2.99 (0.0009)
	S_2	HOMO → LUMO (π,π*)	3.21 (0.7416)
(*E*)-**4e**	S_1	HOMO → LUMO (π,π*)	3.02 (0.6421)
	S_2	HOMO–3 → LUMO (n,π*)	3.18 (0.0000)