Experimental

Materials. Melting points were determined on a micro hot stage apparatus and are uncorrected. 1,3,3-Trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*]pyran] (**1**) and 1,3,3-Trimethylspiro[indoline-2,3'-[3*H*]-naphth[2,1-*b*][1,4]oxazine] (**2**) were purchased from Tokyo Chemical Industry. Slow evaporation of acetone solution of **1** yielded the pale pink single crystals (mp 179 °C), which were used for the photoreactions illustrated in Fig. 1 and X-ray diffraction analysis. Spectral studies of **1** were performed using the purchased microcrystalline powder without purification. The averaged particle size of the powder was 20 μm. Slow evaporation of methanol solution of **2** yielded a mixture of two differently shaped colorless crystals (octahedral and plate), which correspond to the reported dimorphs of **2**.[1] The octahedral single crystals (mp 144 °C) were selected and used for the photoreactions illustrated in Fig. 1 and X-ray diffraction analysis. The octahedral crystals of **2** grown from acetone solution were crushed to microcrystalline powder with particle size ranging from 50 to 100 μm and used for spectral studies. X-ray powder diffraction of the microcrystalline powders of **1** and **2** was measured using a Rigaku MultiFlex powder diffractometer and was confirmed to be identical with the patterns calculated from their crystal structures.

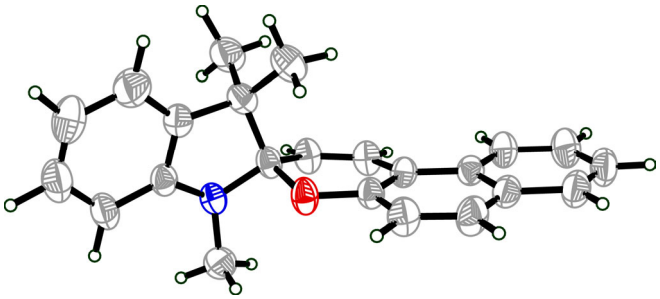
Spectral measurements. Diffuse UV-vis reflectance spectra were measured on a JASCO V-550 spectrometer equipped with an integrating sphere accessory at temperatures between 78 and 300 K, using a liquid nitrogen bath cryostat OXFORD Optistat DN-V with a homemade sample holder. The temperature was held constant within ± 0.1 K during the measurement. NaCl powder (MERCK Suprapur) was ground and used as the reference.

Photoirradiation. A SAN-EI UVF-352S high pressure mercury lamp was used for UV light irradiation. The emission line of 365 nm was isolated by using a band-pass filter (ASAHI Spectra MX0365) and a heat absorption filter (HOYA HA30).

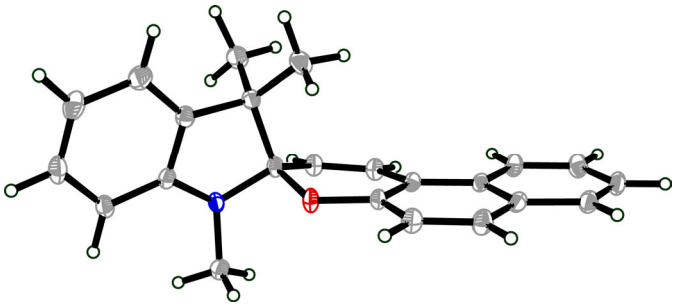
Reference. 1. Millini, R.; Piero, G. D.; Allegrini, P.; Crisci, L.; Malatesta, V. *Acta Crystallogr.* **1991**, *C47*, 2567–2569.

Table S1. Crystal Data and Structure Refinements for **1** and **2**

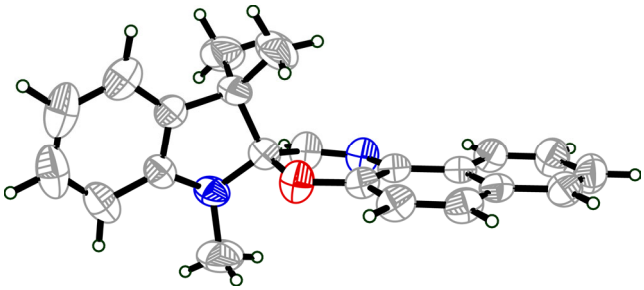
compound	**1**		**2**	
empirical formula	$C_{23}H_{21}NO$		$C_{22}H_{20}N_2O$	
formula weight	327.41		328.40	
temperature (K)	room temperature	90	room temperature	90
crystal system	monoclinic		orthorhombic	
space group	$P2_1/n$		*Pbca*	
color of crystal	pale pink		colorless	
a (Å)	14.6137(12)	14.5329(7)	17.1642(8)	17.275(2)
b (Å)	6.3473(5)	6.2561(3)	16.8250(8)	16.559(2)
c (Å)	19.4928(16)	19.3262(10)	12.4068(6)	12.2061(17)
β (°)	103.501(2)	103.547(1)	90.0	90.0
V (Å^3)	1758.1(2)	1708.24(15)	3582.9(3)	3491.6(8)
Z	4		8	
reflections collected	26272	25364	53515	52107
independent reflections	5123	4986	5238	5101
R_{int}	0.0382	0.0388	0.0258	0.0174
data/restraints/parameters	5123/0/310	4986/0/310	5238/0/306	5101/0/306
goodness-of-fit on F^2	1.024	1.040	1.049	1.056
$R[F^2 > 2\sigma(F^2)]$	0.0531	0.0541	0.0554	0.0448
$wR(F^2)$ (all data)	0.1588	0.1421	0.1645	0.1284
ρ_{min} (e Å^{-3})	-0.160	-0.225	-0.171	-0.172
ρ_{max} (e Å^{-3})	0.270	0.544	0.292	0.509



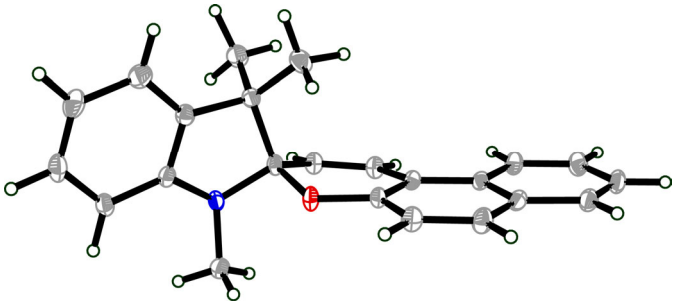
1 at room temperature



1 at 90 K



2 at room temperature



2 at 90 K