Reversal of regioselectivity (straight *vs.* cross ring closure) in the intramolecular [2+2] photocycloaddition of phenanthrene derivatives†

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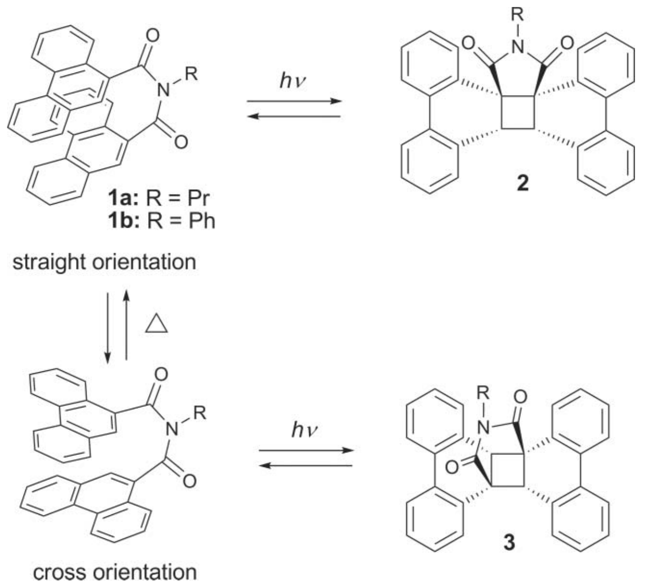
Intramolecular [2+2] photocycloaddition of aromatic chain imides possessing bis-phenanthrene moieties afforded straight and cross ring closure products. The ratio of cycloadducts was dependent on reaction time and temperature, which resulted in a reversal of regioselectivity. The reaction was proved to involve a retro cycloaddition. The cross ring closure products were formed predominantly in the early stage of the reaction at lower reaction temperature. In contrast, the straight ring closure products were predominant at higher reaction temperature with prolonged irradiation.

Introduction

Regio- and stereo-controlled organic photochemical reactions have been studied intensively not only from mechanistic viewpoints but also from a synthetic point of view.[1] The factors generally utilized to affect selectivities are reaction temperature,[2] solvent polarity,[3] irradiation wavelength,[4] excited spin states,[5] and reaction phases.[6] In some cases, high selectivities have been attained including the reversal of the selectivities by varying the above-mentioned conditions. However, the successful examples are limited to diastereoselective [2+2] photocycloadditions. Moreover, the majority of the examples of the reversal of selectivities were reported in the stereoselective Paternò-Büchi reaction.[5,7] In this paper, we present the rare example of the regio-controlled intramolecular [2+2] photocycloaddition reaction with the reversal of regioselectivity depending on the reaction temperature and irradiation time. In addition, the reaction involves a rare example of cross ring closure in intramolecular [2+2] photocycloaddition of aromatic compounds.



Scheme 1 Photocycloaddition of a phenanthrene–phenanthrene system.

Results and discussion

Aromatic chain imides **1** possessing two phenanthrene moieties linked with iminodicarbonyl were subjected for photochemical study. Irradiation of **1** with a high pressure Hg lamp under argon atmosphere through Pyrex filter (>290 nm) resulted in the formation of two cycloadducts **2** and **3** in an almost quantitative yield (Scheme 1). The product ratio varied depending on the reaction temperature and irradiation time. The structure of **2a** and **3a** were unequivocally determined by single crystal X-ray analysis of them. Their X-ray structures are shown in Fig. 1 together with that of **1a** which adopts a cross-oriented conformation. The cycloadducts are regioisomers of the intramolecular [2+2] photocycloaddition. The compound **2a** is the straight ring closure [2+2] cycloadduct and **3a** is the product of cross ring closure.

In general photocycloaddition of a compound possessing two double bonds linked with a propylene chain affords a cyclopentane ring fused cyclobutane derivative *via* the straight ring closure known as the "rule of five" ring closure.[8] The regio chemistry of the cycloadducts was interpreted in terms of the stability of diradical intermediates.[9] In some cases, the cross ring closure[10] were reported. It gives a bicyclo[3.1.1]heptane ring system. Up to now, this cross ring closure is limited to aliphatic [2+2] photocycloaddition. In the photocycloaddition of aliphatic imides, an exclusive formation of cross adducts was reported in the reaction of dimethylacrylimides.[11] Aromatic chromophores, such as naphthalene,[12] phenanthrene,[13] and coumarin[14] have

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† Electronic supplementary information (ESI) available: Spectroscopic data (**1b**, **2b**, **3b**, **4** and **5**) and copies of ^{1}H and ^{13}C NMR spectra. Crystallographic data of **1a**, **2a** and **3a** in CIF format. CCDC reference numbers 759325 (for **1a**), 606845 (for **2a**) and 606846 for (**3a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000179a

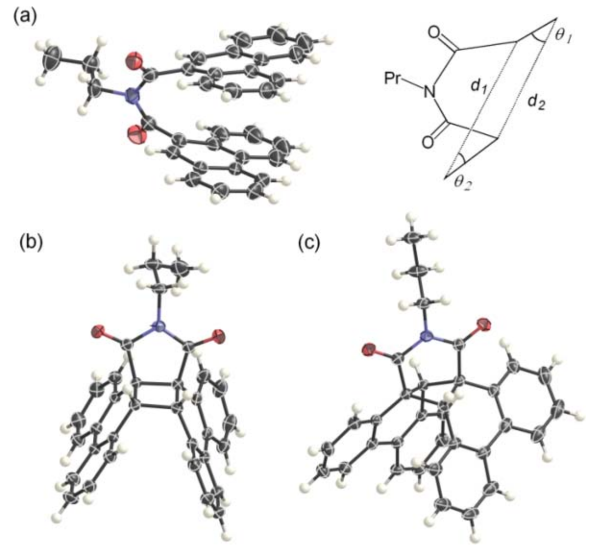


Fig. 1 Single crystal X-ray structure of **1a** (a), **2a** (b) and **3a** (c). Ellipsoids are presented in 50% probability level while isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

been known to give [2+2] photocycloadducts in both inter- and intramolecular ways. To the best of our knowledge, this is the first example of the cross ring closure between aromatic chromophores in intramolecular [2+2] photocycloaddition.

The product ratio was reaction temperature and time dependent (Table 1). Irradiation was carried out in deuterated solvents with bubbling of argon prior to irradiation. The product ratio was determined based on the integration of both products in the reaction mixture by ^{1}H NMR spectroscopy. Both products were generated immediately in the early stage of the reaction with the cross cycloadduct as the major product in the case of **1a**. Even irradiation for 30 s caused completion or almost completion of the reaction (entries 1, 3, and 7). Prolonged irradiation resulted in predominant formation of **2**. The isomer ratios of **2a** : **3a** = 80 : 20 and **2b** : **3b** = 97 : 3 were observed after irradiation for 10 h and 7 h respectively, for **1a** and **1b** in benzene-d_6 at 50 °C (entries 2 and 10). The results indicate the existence of the retro [2+2] photocycloaddition. No other product was found. However, prolonged irradiation in acetone-d_6 or in acetonitrile-d_3 caused slight decomposition. A better yield of the cross adduct **3** was obtained at lower reaction temperature. The isomer ratios of **2a** : **3a** = 23 : 77 and **2b** : **3a** = 32 : 68 were observed for **1a** and **1b**, respectively, after irradiation for 3 min in acetone-d_6 at −78 °C (entries 6 and 12). When the irradiation was carried out in a melted state at 230~260 °C, the cycloadduct **2a** was the sole product (entry 8). No reaction occurred in solid state at ambient temperature. Because of the cross-oriented conformation of **1a** observed in its X-ray structure (Fig. 1a), it is difficult to cyclise in the 1,5-cycloaddition manner. Even though the distances between the two carbon atoms (d_1 and d_2) to be reacted in the 1,6-cycloaddition are both 3.3 Å which is within the distance allowed for cycloaddition in Schmidt rule,[15] the angles between the double bond (θ_1 and θ_2) are rather narrow (58°).

Table 1 Temperature dependent product ratios in the photocycloaddition of **1**[a]

Entry	compd.	Solvent	Temp./ °C[b]	Time/ min[c]	Ratio (**2a** : **3a**)	Conversion (%)
1	**1a**	C_6D_6	50	0.5	37 : 63	100
2	**1a**	C_6D_6	50	600	80 : 20	100
3	**1a**	$(CD_3)_2CO$	50	0.5	44 : 56	85
4	**1a**	$(CD_3)_2CO$	50	3	48 : 52	100
5	**1a**	$(CD_3)_2CO$	0	3	40 : 60	100
6	**1a**	$(CD_3)_2CO$	−78	3	23 : 77	85
7	**1a**	CD_3CN	50	0.5	42 : 58	90
8	**1a**	melted state	230~260	5	100 : 0	46
9	**1b**	C_6D_6	50	0.5	71 : 29	70
10	**1b**	C_6D_6	50	420	97 : 3	100
11	**1b**	$(CD_3)_2CO$	−78	1	30 : 70	53
12	**1b**	$(CD_3)_2CO$	−78	3	32 : 68	100

[a] Irradiation was carried out with a high pressure Hg lamp under argon atmosphere through Pyrex filter (>290 nm). The regioisomer ratio was determined by ^{1}H NMR spectroscopy. The concentration of **1a**: *ca.* 10^{-2}M. [b] Reaction temperature. [c] Irradiation time

The reaction profile of the photoreaction of **1a** at 50 °C in benzene-d_6 was monitored by ^{1}H NMR spectroscopy (Fig. 2a). It showed that both products were generated immediately. The amount of **3a** decreased and that of **2a** increased gradually with increasing irradiation time. The results clearly show that the reaction involves retro [2+2] photocycloaddition of **3a** to give **2a**. Prolonged irradiation resulted in the photo stationary state with the ratio of **2a** : **3a** = 80 : 20. The cycloadducts **2a** and **3a** are thermally stable. Heating of them for a day at 50 °C in the dark caused no interconversion. In order to confirm this, the photoreaction of **2a** and **3a** were carried out independently under the identical photoreaction conditions. Irradiation of **2a** resulted in the immediate formation of **3a**. Formation of **1a** was not detected. Then, the amount of **3a** decreased and that of **2a** increased gradually with increasing irradiation time. Finally it reached to the photo stationary state with the identical isomer ratio as started from **1a** (Fig. 2b). Similarly, irradiation of **3a** afforded the same isomer ratio at the photo stationary state (Fig. 2c). The results indicate that the reaction involves the retro cycloadditions of both **2a** and **3a**. Equilibrium exists under irradiation. The reaction profiles of **1a** and **2a** are unusual as those involving an equilibration. Normally, both products should be generated with a constant ratio all through the reaction period in an equilibration. The amount of **3a** should not jump in the early stage of the reaction and after that it should not decrease if the reaction involves equilibrium. Nevertheless the photo stationary state exists in the reaction. The same product ratio was obtained starting from any of **1a**, **2a** and **3a**. The explanation for this observation was found from the inspection of their UV spectra. Fig. 3 shows the uv spectra of **1a**, **2a** and **3a**. The absorption of **2a** and **3a** over 300 nm, the region covers the line spectrum (313 nm) emitted from a high pressure Hg lamp, is weaker than that of **1a**. Therefore, most of the light will be absorbed by **1a**. Because of this, the photocycloaddition of **1a** is much more efficient than the retro cycloadditions of **2a** and **3a** in the early stage of the reaction, which results in the immediate formation of the favourable product **3a**. While the reaction proceeds the amount of **3a** gradually decreases and finally it reaches to the photo stationary state after the irradiation of a reasonably long period of time. In the case of the retro cycloaddition of **2a**, the resulting **1a** is immediately converted to **3a** which will be accumulated in the beginning of the reaction and after that the reaction proceeds in a similar way as observed in the reaction profile of **1a**.

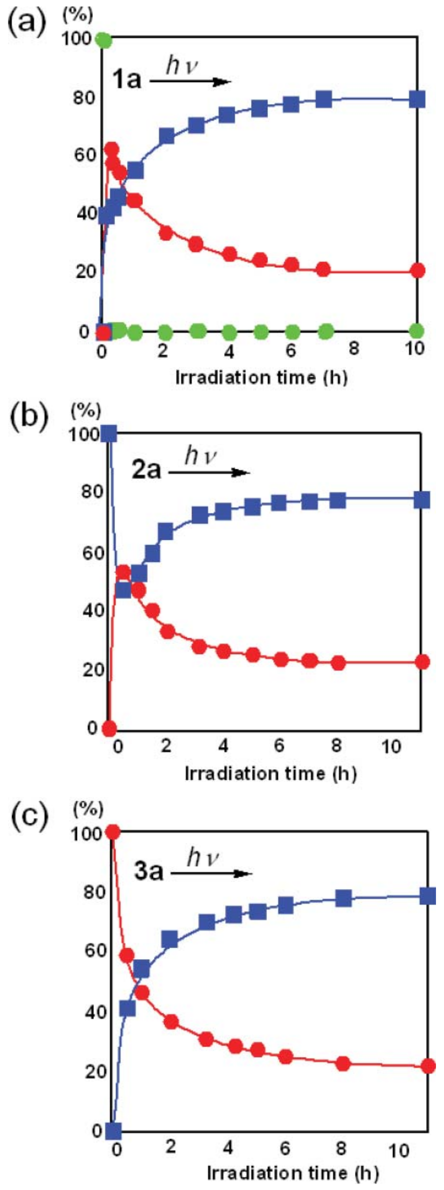


Fig. 2 Reaction profiles of the photoreaction of **1a** (a), **2a** (b) and **3a** (c) in benzene-d_6 at 50 °C monitored by ^{1}H NMR spectroscopy. Green circles, blue squares, and red circles indicate the progress of the reaction for **1a**, **2a** and **3a**, respectively.

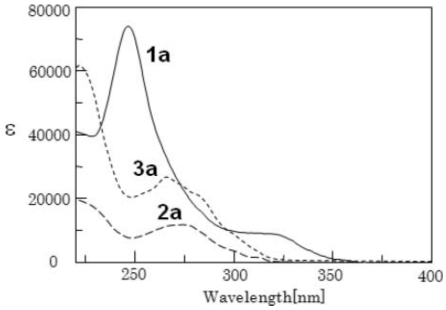


Fig. 3 Absorption spectra of **1a**, **2a** and **3a** in acetonitrile.

In order to exclude the retro cycloaddition, selective excitation of **1a** was examined. Independent irradiation of **1a**, **2a** and **3a** was carried out with high pressure Hg lamp through combination of glass filters (340 nm < λ < 390 nm) to choose the line spectra at 365/366 nm for excitation. Both cycloadducts **2a** and **3a** were inert within experimental errors at the early stage of the reaction (irradiation for 3 min) while 95% of **1a** was reacted in the same irradiation period. However, prolonged irradiation (3 h) of **2a** and **3a** caused reaction with conversion of 19 and 38%, respectively. Because of the existence of slight absorption of **2a** and **3a** at this wavelength, they reacted slowly.

The conformation of **1** is responsible for the regiochemistry of the cycloadducts. If the orientation of two phenanthrene moieties is parallel (straight orientation), then the straight ring closure occurs to give **2**. On the contrary, the cross orientation of them affords the cross ring closure adduct **3** as shown in Scheme 1. It is reasonable to consider that the reactivity of these conformations should be responsible for the regioselectivity. The cross oriented **1** should be more stable than the straight oriented **1**. In order to survey the relative stability of the starting conformations, the DFT (B3LYP/6-31G(d)) calculation was carried out using the Gaussian 03 program package.[16] It is calculated that the cross-oriented conformations of **1a** and **1b** are more stable than those of the corresponding straight-oriented conformations in 2.3 and 2.4 kcal mol^{-1}, respectively. To investigate the conformational change between them, a variable temperature ^{1}H NMR study of **1a** in $CDCl_3$ was carried out. Lowering the temperature down to 218 K no spectral change of the aromatic protons was observed except slight broadening of them. The results indicate that conformational change of the phenanthryl moieties was not restricted at this temperature.

The mechanism of the photodimerization of phenanthrene derivatives was well investigated by Lewis *et al.*[17] Depending on the electron-withdrawing substituents at the 9-position of phenanthrene, they found three types of reactions. Methyl phenanthrene-9-carboxylate undergoes self-quenching and dimerization *via* normal excimer mechanism, *N*,*N*-dimethylphenanthrene fails to undergo either self-quenching or photodimerization and 9-cyanophenanthrene fails to undergo self-quenching and undergoes dimerization predominantly *via* excitation of a ground-state π-complex. In our case, fluorescence self-quenching was observed for **1a** and **1b**. They are completely non-fluorescent in a dilute solution. This is due to the tethered structure of them. Self-quenching easily occurs between the facing phenanthrene moieties. Our results, the occurrence of self-quenching and dimerization, indicated the possible involvement of normal excimer mechanism for their dimerization.

In order to elucidate the excited states of the retro cycloaddition, the photochemical reactions of **1a**, **2a** and **3a** were carried out with a triplet sensitizer. Irradiation was performed with benzophenone or Michler's ketone with high pressure Hg lamp through combination of glass filters (340 nm < λ < 390 nm) using a merry-go-round apparatus. The results are shown in Table 2. Without a sensitizer, no or almost no retro reaction occurred for **2a** and **3b**, respectively, because the reaction was still in the early stage. The intensity of light for irradiation was extremely reduced compared to that utilized in the above-mentioned selective irradiation experiments through filters. In contrast to the non-sensitized reaction, the formation of **1a** was observed in the sensitized reaction of **2a** and **3a**. The results indicate that the retro cycloaddition proceeds *via* triplet excited state. The appearance of

Table 2 Product ratios in the photosensitized reactions at photo stationary state[a]

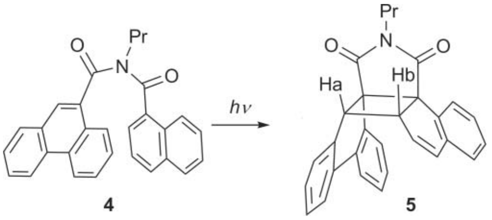
Starting material	Sensitizer[b]	Product ratio **1a** : **2a** : **3a**
1a	None	0 : 38 : 62
1a	A	15 : 40 : 45
1a	B	88 : 10 : 2
2a	None	0 : 100 : 0
2a	A	17 : 43 : 41
2a	B	87 : 12 : 1
3a	None	0 : 4 : 96
3a	A	17 : 37 : 46
3a	B	87 : 9 : 4

[a] Irradiation ($340\ \text{nm} < \lambda < 390\ \text{nm}$) was carried out for 8 h in benzene-d_6 at *ca.* 20 °C. [b] With one equivalent amount of benzophenone (A) or Michler's ketone (B).

1a in the reactions of **2a** and **3a** also indicates that the cycloaddition of **1a** involves singlet excited state, because **1a** was completely consumed in the reaction of **1a**.

As the intermediates of photocycloaddition[18,19] we postulate diradicals *via* the stepwise mechanism. A diradical intermediate was proposed by us in the similar photocycloaddition of naphthalene derivatives in which the diradical intermediate was trapped by molecular oxygen to afford a novel 1,8-endoperoxide.[19]

It is noteworthy to mention that photocycloaddition of the imide possessing phenanthrene and naphthalene moieties **4** afforded an exclusive formation of the [2+2] cycloadduct **5** *via* the straight ring closure (Scheme 2). The structure of **5** was determined based on the *cis* coupling constant between protons H_a and H_b (8.9 Hz). The conjugation by the extra phenylene ring in **1** could stabilise the diradical intermediate leading to the cross cycloadduct **3**. However, the stability of the diradical intermediate responsible for the formation of the cross cycloadduct might not be enough in the case of **4**. This could be the reason why we observed the cross [2+2] photocycloaddition in the phenanthrene–phenanthrene and not in the phenanthrene–naphthalene system.



Scheme 2 Photocycloaddition of a phenanthrene–naphthalene system.

Conclusion

We have demonstrated a novel example of intramolecular cross [2+2] photocycloaddition of aromatic compounds and an unusual reversal of regioselectivity affected by reaction temperature and irradiation time. The straight and cross cycloadducts were obtained preferably at higher and lower reaction temperature, respectively.

Experimental

1 General methods

All reactions were performed under nitrogen atmosphere. All commercially available reagents were used without further purification. All solvents used were special grade. Column chromatography was performed with silica gel (0.063–0.2 mm). Solvents were evaporated under reduced pressure. All yields given refer to as isolated yields. Melting points were uncorrected. NMR spectra were recorded on 300 and 500 MHz spectrometers. MS experiments were performed on high resolution magnetic sector mass spectrometers. Crystallographic data were collected on a CCD detector with graphite monocromated Mo-Kα ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods SHELXS-97 and refined by full-matrix least-squares SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions.

2 Synthesis of *N*-(phenanthrene-9-carbonyl)-*N*-propyl-phenanthrene-9-carboxamide (1a)

To a solution of *N*-propyl-9-phenathrylcarboxamide (302 mg, 1.15 mmol), triethyl amine (0.15 mL, 2.03 mmol), and DMAP (14 mg, 0.11 mmol) in toluene (40 mL) was added a toluene solution (10 mL) of phenantroyl chloride prepared from the reaction of phenanthroic acid (305 mg, 1.37 mmol) and thionyl chloride. After addition of toluene (15 mL), the resulting mixture was refluxed for a day and was quenched with aqueous 1 N HCl solution. Ethyl acetate (100 mL) was added to this solution and the resulting organic layer was separated and washed with saturated aqueous solution of $NaHCO_3$. After drying over anhydrous $MgSO_4$, solvent was evaporated and the residue was chromatographed on silica gel eluted with hexane–ethyl acetate (3/1) to afford 262 mg (49%) of **1a** as a colourless crystal. Mp: 168–170 °C (ethyl acetate–hexane); UV-vis (CH_3CN) 247 (74100), 312 (sh) nm (9190); IR (KBr) 3044 (w), 2956 (w), 1707 (m), 1657 (s), 1449 (m) 1337 (m) cm^{-1}; (500 MHz, $CDCl_3$) δ 1.26 (q, J = 7.5 Hz, 3H), 2.14 (sext, J = 7.5, 2H), 4.32 (t, J = 7.5 Hz, 2H), 7.06 (td, J = 7.3, 1.5 Hz, 2H), 7.09 (td, J = 7.3, 1.5 Hz, 2H), 7.36 (td, J = 7.4, 1.3 Hz, 2H), 7.40 (td, J = 7.5, 1.6 Hz, 2H), 7.47 (s, 2H), 7.49 (dd, J = 7.6, 1.6 Hz, 2H), 7.77 (dd, J = 8.0, 1.5 Hz, 2H), 7.95 (dd, J = 8.0, 1.5 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz) δ 11.9, 22.3, 47.0, 121.83, 121.85, 125.4, 126.36, 126.44, 126.7, 127.0, 127.4, 127.7, 129.0, 129.2, 129.4, 130.3, 133.9, 173.6; HRMS (FAB), calcd for $C_{33}H_{25}NO_2$ (M^+) 467.1885, found 467.1849. Crystal data for **1a**: $C_{33}H_{25}NO_2$, M = 467.54, Orthorhombic, space group $Pna2_1$ (no. 33), a = 9.489(2), b = 27.726(5), c = 9.063(2), V = 2384.5(8) Å^3, Z = 4, T = 200 K, D_c = 1.302 Mg m^{-3}, μ = 0.080 mm^{-1}, 11320 reflections measured, 4220 unique (R_{int} = 0.0336) which were used in all calculations. The final R_1 and wR_2 were 0.0487 and 0.0860 (all data). CCDC 759325.†

3 Photocycloaddition

3.1 Photocycloaddition of 1a. Acetone solution (25 mL) of **1a** (85 mg, 0.18 mmol) was irradiated with a 450 W high-pressure Hg lamp under argon atmosphere through Pyrex filter for 2 h at −78 °C. After evaporation of solvent, the residue was chromatographed on silica gel eluted with hexane–ethyl acetate (5/1) to give **2a** (20 mg, 24%) and **3a** (56 mg, 66%) as colourless crystals. Cycloadduct **2a**: Mp: 204–206 °C (colorless crystals from ethyl acetate–hexane); UV-vis (CH_3CN) 274 nm (11900); IR (KBr) 3072 (w), 2964 (w), 1771 (m), 1702 (s), 1390 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, J = 7.4 Hz, 3H), 1.93 (sext, J = 7.4 Hz, 2H), 3.85 (t, J = 7.4 Hz, 2H), 4.48 (s, 2H), 6.55 (dd, J = 7.6, 1.2 Hz, 2H), 6.75 (dd, J = 7.6, 1.2 Hz, 2H), 6.95 (td, J = 7.6, 1.2 Hz, 2H), 6.96 (td, J = 7.6, 1.2 Hz, 2H), 7.04 (td, J = 7.6, 1.4 Hz, 2H), 7.10 (td, J = 7.6, 1.4 Hz, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 21.4, 41.3, 46.3, 58.7, 122.8, 122.9, 127.3, 127.40, 127.43, 128.3, 128.4, 129.5, 130.0, 132.1, 133.9, 179.4; HRMS (FAB), calcd for $C_{33}H_{25}NO_2$ (M^+) 467.1885, found 467.1872. Crystal data for **2a**: $C_{33}H_{25}NO_2$, M = 467.54, Monoclinic, space group $P2_1/n$ (no. 14), a = 13.0567(1), b = 9.2544(1), c = 19.7847(2), β = 100.23°, V = 2352.65(4) Å^3, Z = 4, T = 150 K, D_c = 1.320 Mg m^{-3}, μ = 0.082 mm^{-1}, 26400 reflections measured, 4812 unique (R_{int} = 0.0268) which were used in all calculations. The final R_1 and wR_2 were 0.0487, wR_2 = 0.0925 (all data). CCDC 606845.†

Cycloadduct **3a**: Mp: 209–212 °C (colorless crystals from ethyl acetate–hexane); UV-vis (CH_3CN) 267 nm (26700); IR (KBr) 3064 (w), 2963 (w), 1740 (m), 1685 (s), 1447 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (t, J = 7.4 Hz, 3H), 1.80 (sext, J = 7.4 Hz, 2H), 3.97 (dt, J = 13.2, 7.4 Hz, 1H), 4.05 (dt, J = 13.2, 7.4 Hz, 1H), 4.23 (s, 2H), 6.04 (d, J = 7.7 Hz, 2H), 6.59 (td, J = 7.5, 0.9 Hz, 2H), 6.86 (td, J = 7.6, 1.0 Hz, 2H), 7.29 (d, J = 7.7 Hz, 2H), 7.34 (td, J = 7.6, 1.6 Hz, 2H), 7.42 (td, J = 7.7, 1.2 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 8.03 (dd, J = 7.7, 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.5, 21.4, 41.3, 52.4, 54.0, 122.2, 123.0, 126.5, 126.9, 127.0, 127.6, 128.4, 128.6, 128.7, 129.9, 132.2, 134.4, 175.1; HRMS (FAB), calcd for $C_{33}H_{25}NO_2$ (M^+) 467.1885, found 467.1879. Crystal Data for **3a**: $C_{33}H_{25}NO_2$, M = 467.54, Orthorhombic space group $P2_12_12_1$ (no. 19), a = 12.473(1), b = 13.377(1), c = 13.888(1), V = 2317.3(4) Å^3, Z = 4, T = 150 K, D_c = 1.340 Mg m^{-3}, μ = 0.083 mm^{-1}, 13053 reflections measured, 5198 unique (R_{int} = 0.0324) which were used in all calculations. The final R_1 and wR_2 were 0.0437 and 0.0900 (all data). CCDC 606846.†

3.2 Analytical photocycloaddition of 1. Imide **1** was dissolved in deuterated solvent (*ca.* 10^{-2} M) and was irradiated with a 450 W high-pressure Hg lamp. Prior to irradiation argon gas was bubbled into the solution for 20 min. After appropriate duration under irradiation, ^1H-NMR spectra of the reaction mixtures were recorded and the product ratios were determined based on their integrals.

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