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Intramolecular 10,10a-[2+2] photocycloaddition reactions of phenanthrenes with linked styrene

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ABSTRACT

Intramolecular photocycloaddition reactions of styrene linked 9-cyanophenanthrenes led to formation of C-9 C-10 [2+2] cycloadducts which underwent cycloreversion under the prolonged irradiation conditions to regenerate the starting substrates. Unusual 8-membered ring products were irreversibly formed in these processes. Product distributions were governed by substituent controlled, donor-acceptor interactions that direct generation of two intramolecular singlet exciplexes, which serve as intermediates in the pathways to formation of 9,10- and 10,10a-[2+2] adducts.

1. Introduction

Photocycloaddition reactions between arenes and unsaturated compounds represent powerful methods for the construction of polycyclic compounds [1–3]. Although many stereo- and regio-specific photocycloaddition reactions of alkenes with phenanthrenes and naphthalenes have been described, the sites at which reactions have been observed to take place are limited to the 9,10-positions of phenanthrenes [4–22], and the 1,2- and 1,4-positions of naphthalenes [23–38]. The ability to alter the arene sites at which photocycloaddition reactions occur should greatly benefit the synthetic potential of these processes and enhance the understanding of the structures and reactivities of exciplexes that are intermediates in these reactions.

Earlier, Kubo et al. uncovered an unusual intermolecular [3+2] photocycloaddition reaction of alkenes to naphthalene that result in the formation of 1,8-adducts [39,40], and later discovered photoprocesses that lead to generation of 8,9-phenanthrene cycloadducts [41]. However, until now no photocycloaddition reactions of alkenes taking place at the 10,10a-position of phenanthrene have been observed, although the corresponding 1.8a-addition of naphthalene has been observed [42–44]. Based on the fact that intramolecular photochemical reactions are often both highly efficient and stereoselective, we have recently designed linked alkene-naphthalene substances that undergo intramolecular photocycloaddition at the 1,3-position of the naphthalene ring [45], and also observed that efficient, site-selective photocycloaddition reactions occur in alkene-pyrene linked systems [46]. In the effort described below, we have uncovered an unprecedented intramolecular photocycloaddition process that transforms tethered phenanthrene-styrene substrates to unexpected eight-membered ring products along with normal 9,10-[2+2] cycloadducts. The former process takes place via an initial and unusual 10,10a-[2+2] photocycloaddition reaction which produces a cycloadduct that undergoes thermal electrocyclic ring opening to generate the observed eight membered ring product.

2. Results and discussion

Irradiation of a benzene solution containing 9-cyano-10-phenanthrylmethyl cinnamyl ether (*trans*-**1a**) in a Pyrex vessel (>280 nm light) under an argon atmosphere by using a high-pressure mercury lamp gave rise to efficient formation of two cycloadducts **2a** and **3a** (Scheme 1). These products were isolated by using silica gel column chromatography. The structures of the photoproducts were first assigned by using spectroscopic methods

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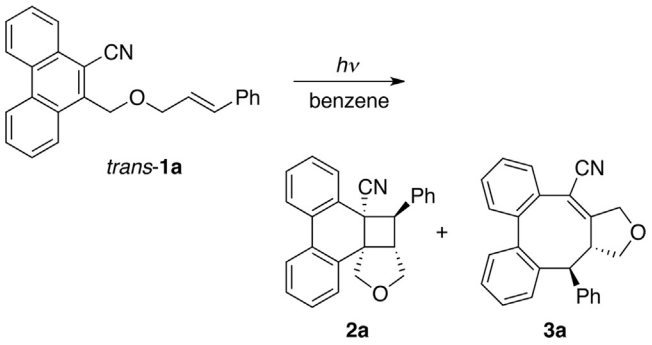


Scheme 1. Intramolecular Photocycloaddition of 9-Cyano-10-phenanthrylmethyl Cinnamyl Ether (*trans*-**1a**).

and then unambiguously determined by using X-ray crystallographic analysis (Figs. 1 and 2). The cyclobutane ring containing product **2a** is an expected result of intramolecular [2+2] photocycloaddition of the styrene moiety at the reactive 9,10-positions of the phenanthrene group. In contrast, product **3a** is unusual in that it contains an eight-membered ring whose origin is interesting.

Substituents on the styrene and phenanthrene groups were found to govern the distribution of products produced in this process (Scheme 2, Table 1). Intramolecular [2+2] photocycloaddition proceeded when a solution of the 6-cyano derivative *trans*-**1b** was photoirradiated, but the eight-membered ring product **3b** was not generated (entries 5 and 6). Photoreaction of *trans*-**1c**, a substance that does not have a 9-cyano substituent on the phenanthrene ring, did not react to yield **3c**, but it slowly was transformed to **2c** along with the isomerized reactant *cis*-**1c** (entries 7 and 8). In addition, the *p*-methoxy- and 9-cyano substituted substrate *trans*-**1d** photoreacted to afford **2d** exclusively (entries 9 and 10). Moreover, the substrate *trans*-**1e**, possessing cyano groups at both the *para* and 9-positions underwent efficient reaction to produce the eight-membered ring product **3e** (entries 11–13). Finally, the *p*-cyano, 9-cyano, and 3-methoxy substituted derivative *trans*-**1f** participated in high yielding photoreaction to form the eight-membered ring adduct **3f** exclusively (entry 14).

The results of a study of product distributions as a function of reactant conversion showed that **2a** was formed at the initial stage of the photoreaction (10 min) of *trans*-**1a** to the total exclusion of

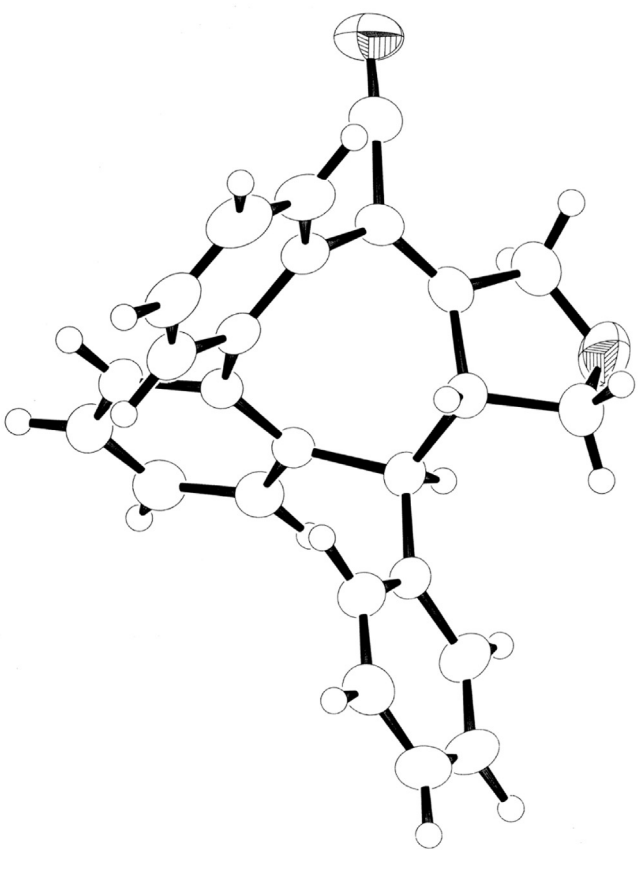


Fig. 2. ORTEP drawing of **3a**. $C_{25}H_{19}NO$, monoclinic, $P2_1/n$ (#14), $Z = 4$, $a = 9.934(4)$ Å, $b = 12.740(4)$ Å, $c = 14.430(7)$ Å, $\beta = 96.18(4)^\circ$, $D_{calcd} = 1.278$ g/cm^3, $\mu = 0.773$, $R = 0.040$, $R_w = 0.041$, GOF = 1.827.

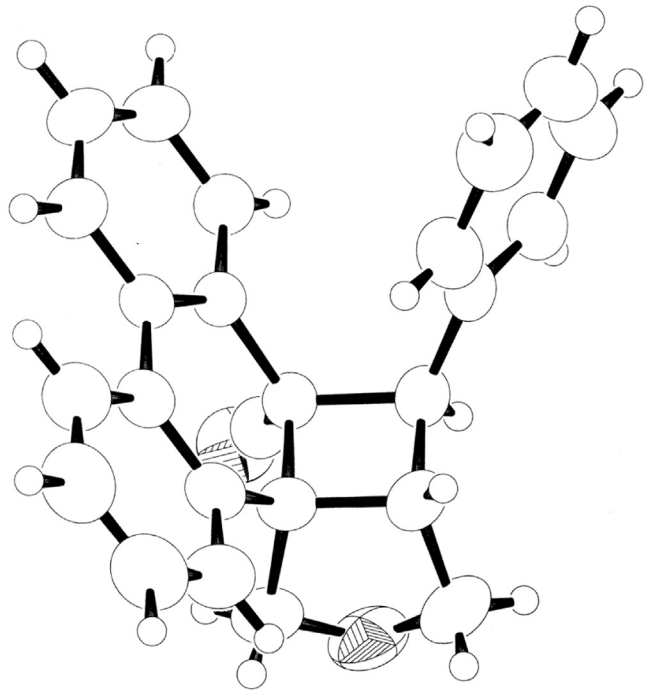
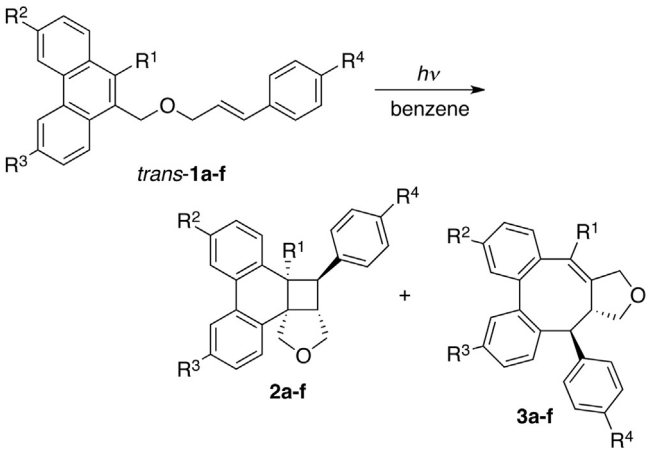


Fig. 1. ORTEP drawing of **2a**. $C_{25}H_{19}NO$, monoclinic, $P2_1/c$ (#14), $Z = 8$, $a = 15.526(2)$ Å, $b = 15.428(3)$ Å, $c = 16.707(2)$ Å, $\beta = 113.092(7)^\circ$, $D_{calcd} = 1.261$ g/cm^3, $\mu = 0.763$, $R = 0.045$, $R_w = 0.049$, GOF = 1.883.



Scheme 2. Intramolecular Photocycloaddition Reactions of Linked Styrene-Phenathrenes.

Table 1
Effects of Substituents and Irradiation Time on the Intramolecular Photocycloaddition Reactions of Linked Styrene-Phenathrenes.[a]

Entry	**1**					Irradiation time	Yields (%)		
		R^1	R^2	R^3	R^4		**2**	**3**	*cis*-**1**[b]
1	*trans*-**1a**	CN	H	H	H	10 min	78	tr[c]	0
2	*trans*-**1a**	CN	H	H	H	1 h	89	3	0
3	*trans*-**1a**	CN	H	H	H	12 h	83	10	0
4	*trans*-**1a**	CN	H	H	H	24 h	47	46	0
5	*trans*-**1b**	H	CN	H	H	10 min	66	0	0
6	*trans*-**1b**	H	CN	H	H	12 h	80	0	0
7	*trans*-**1c**	H	H	H	H	10 min	13	0	11
8	*trans*-**1c**	H	H	H	H	1 h	21	0	20
9	*trans*-**1d**	CN	H	H	OMe	10 min	79	0	0
10	*trans*-**1d**	CN	H	H	OMe	12 h	90	tr[c]	0
11	*trans*-**1e**	CN	H	H	CN	10 min	79	3	0
12	*trans*-**1e**	CN	H	H	CN	1 h	74	21	0
13	*trans*-**1e**	CN	H	H	CN	12 h	tr[c]	>98	0
14	*trans*-**1f**	CN	H	OMe	CN	3 h	0	>98	0

[a] The photoreaction of *trans*-**1** (0.03 mmol) (>280 nm light using Pyrex vessel) was carried out in benzene-d_6 (0.6 mL) under argon atmosphere. The yields were determined by ^{1}H NMR spectra.
[b] *cis*-isomer of *trans*-**1**.
[c] Trace.

3a, but at longer irradiation times its yield decreased and that of **3a** increased (Table 1, entries 1–4). Monitoring the course of this reaction by using UV absorption spectroscopy showed that a simultaneous decrease and increase in the respective bands of *trans*-**1a** and **2a** took place associated with the appearance of isosbestic points (Fig. 3). Importantly, **2a** was found to undergo cycloreversion to form *trans*-**1a** under the reaction conditions, but the eight membered ring product **3a** did not, thus explaining observations made in exploring the irradiation time course of this process.

Cycloadducts **2a** and **3a** were not produced when 0.1 mol/dm^3 of Michler's ketone (E_T = 275 kJ/mol [47]) was included as a triplet sensitizer in the photoreaction mixture (E_T(9-cyanophenanthrene) = 243 kJ/mol [48]) and the cycloaddition reaction was not quenched by addition of 0.5 mol/dm^3 of the triplet quenchers 2-methyl-1,3-butadiene (E_T = 251 kJ/mol [47]) and dioxygen.

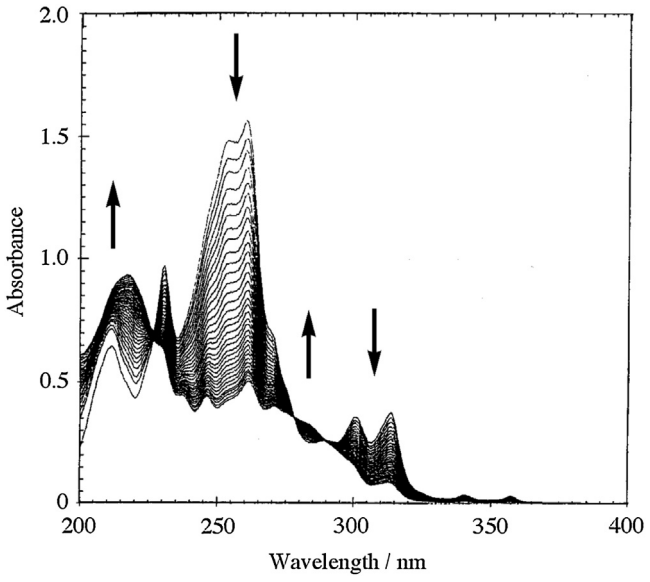


Fig. 3. Time-dependent UV absorption spectra in the intramolecular photocycloaddition of *trans*-**1a** in cyclohexane.

The relative intensities of the fluorescence bands of *trans*-**1a** and *trans*-**1c** in cyclohexane were smaller than those of phenanthrene and 9-cyanophenanthrene (Fig. 4). This observation is a consequence of intramolecular quenching of the singlet phenanthrene excited state by the cinnamyl group. In the fluorescence spectra of *trans*-**1a** and *trans*-**1c**, weak intramolecular exciplex emissions were observed. Fluorescence lifetime measurements with *trans*-**1a** in cyclohexane, by using single photon counting, showed that a major short-lived, transient (<2 ns) was produced, which assigned to the 9-cyanophenanthrene singlet, and a minor long-lived (15 ns) transient corresponding to the singlet exciplex was also formed.

The observations described above have led to the plausible mechanism for these photoreactions given in Scheme 3. Two sandwich-type intramolecular singlet exciplexes, **4** and **5**, produced via phenanthrene excited singlet states, are postulated to serve as reactive intermediates in these photoreactions. The normal [2+2] photocycloadducts **2** are produced by cycloaddition in the exciplexes **4** whereas exciplexes **5** react to generate the strained 10,10a-[2+2] photocycloadducts **6**. Thermal electrocyclic ring opening of **6** then affords the 8-membered ring products **3**. *Cis*/*trans* isomerization of the styrene moiety in the reactants might take place by way of reversible formation and cycloreversion of **2**.

The donor-acceptor effects caused by substituents on the nature of this process are interesting. Compared to the phenyl group in *trans*-**1a**, that of *trans*-**1b** should more favor overlap with the phenanthrene A ring owing to the presence of the 6-cyano group. In the unsubstituted substrate, *trans*-**1c**, the formation of a singlet exciplex is less advantageous because of donor-acceptor interactions, a proposal that is supported by the observation that this substance displays a lower degree of intramolecular fluorescence quenching than that of its analogs. The importance of the donor-acceptor interactions between the styrene aryl group and the phenanthrene A or C rings is also demonstrated by the results of photoreactions of *trans*-**1d** and *trans*-**1e**. Specifically, the observations are consistent with the proposal that the electron-rich aryl group in *trans*-**1d** tends to interact more strongly with the electron-poor A ring in phenanthrene, whereas the electron poor aryl group in *trans*-**1e** in contrast interacts more favorably with the C ring.

The proposals offered above have prompted the design of a substrate that would be more likely to undergo the 10,10a- rather than 9,10-[2+2] photocycloaddtion. This substance, *trans*-**1f**, contains electron withdrawing cyano groups at C-9 of the phenanthrene and the *para* position of the benzene ring and an electron donating methoxy group in the phenanthrene C-ring. As

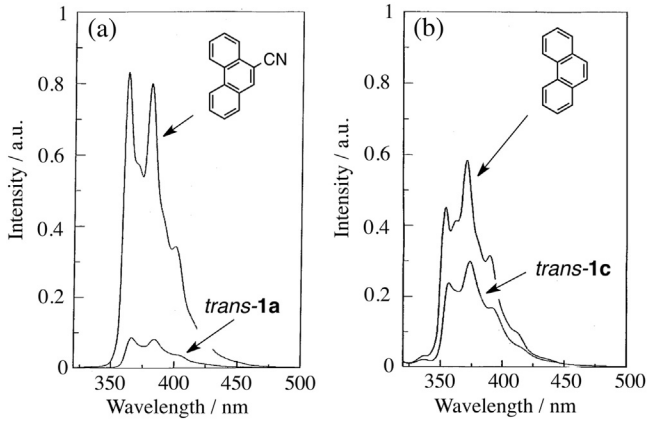
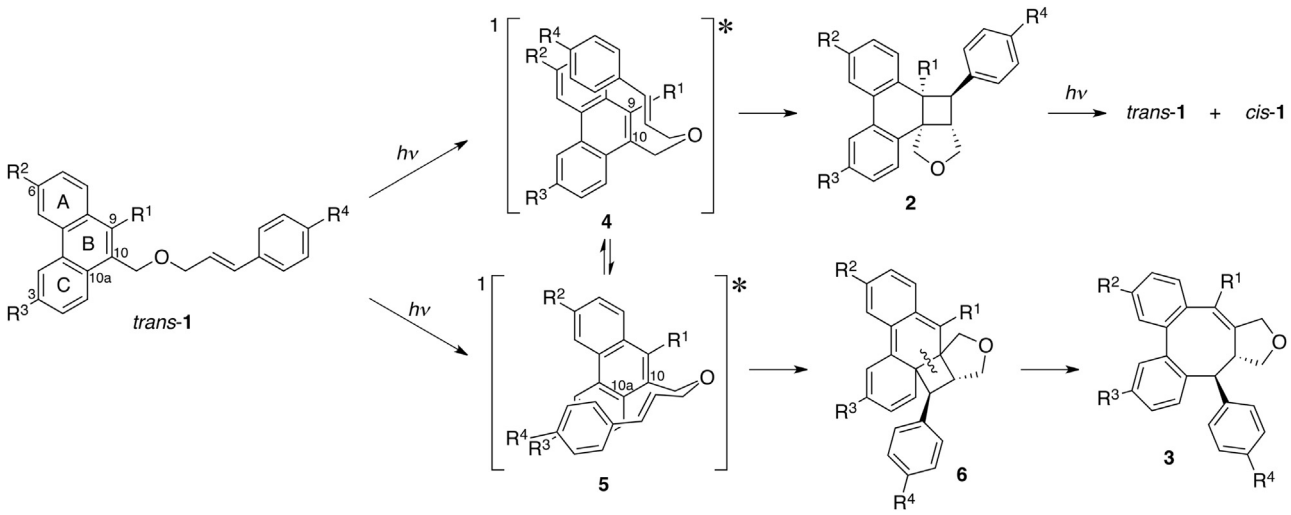


Fig. 4. Fluorescence spectra of (a) 9-cyanophenanthrene and *trans*-**1a**, (b) phenanthrene and *trans*-**1c**, in cyclohexane (1×10^{-5} M).



Scheme 3. Proposed Mechanism for Intramolecular Photocycloadditions in Linked Phenanthrene-Styrene Systems.

described above, photoreaction of this substance yields the eight-membered ring product **3f** exclusively (Table 1, entry 14).

3. Conclusion

Although many intermolecular [4–18] and intramolecular [19–22] photocycloaddition reactions of alkenes taking place at the 9,10-position of phenanthrenes have been reported, those that take place at the 10,10a-position have not been described previously. Thus, the photochemical processes described above are unique in that they demonstrate the operation of a new type of excited state reaction that invloves cycloaddition across the 10,10a-positions of phenanthrene. Moreover, the results of this effort show that the direction of the reaction pathway to the 9,10 or 10,10a position can be controlled by the substituent effects in singlet intramolecular exciplexes.

4. Experimental

4.1. Materials and equipment

CH_3CN was distilled from CaH_2 and then from P_2O_5. Benzene was distilled from P_2O_5 and then from Na. THF was distilled from CaH_2 and then from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. *N*-Bromosuccinimide was recrystallized from hot H_2O. CCl_4, hexane, and *N*-methylpyrrolidone were used as purchased. ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-GX270 (270 MHz and 68 MHz, respectively) or a Varian MERCURY-300 (300 MHz and 75 MHz, respectively) spectrometers with Me_4Si as an internal standard. IR spectra were determined using a Jasco FT/IR-230 spectrometer. UV–vis spectra were recorded using a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were recorded using a Jasco FP-770 spectrophotometer. Mass spectra (EI) were taken on a SHIMADZU GCMS-QP5050 operating in the electron impact mode (70 eV) equipped with GC-17A and DB-5MS column (J&W Scientific Inc., Serial: 8696181). HPLC separations were performed on a recycling preparative HPLC equipped with Jasco PU-986 pump, Shodex RI-72 differential refractometer, Megapak GEL 201Cp and 201CP columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted by using Wako-gel C-70-230 and C-300. X-ray crystallographic data for a single crystals were obtained using a Rigaku AFC5 R or Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. The structures were solved by direct methods (SIR92) and expanded by using Fourier techniques. Calculations were performed using the Texsan or Crystal Structure crystallographic software packages.

4.2. Preparation of 9-cyano-10-phenanthrylmethyl trans-3′-phenyl-2′-propenyl ether (trans-**1a**)

To a THF (100 mL) solution of 9-bromophenanthrene (7.72 g, 30.03 mmol) was slowly added *n*-BuLi (1.6 M hexane solution, 20 mL) at −70 °C under argon atmosphere and stirred for 1 h. MeI (21.318 g, 150.13 mmol) was slowly added and warmed to room temperature. H_2O and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from CH_2Cl_2–*n*-hexane gave 9-methylphenanthrene (5.049 g, 88% yield). Colorless solid; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.72 (s, 3H), 7.52–7.66 (m, 5H), 7.80 (m, 1H), 8.05 (m, 1H), 8.71 (m, 2H) ppm. To a CCl_4 (40 mL) solution of 9-methylphenanthrene (13.00 g, 67.6 mmol) was slowly added CCl_4 (20 mL) solution of Br_2 (11.88 g, 74.4 mmol) at 0 °C and stirred for 2 h. H_2O then 10% NaOH aq were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from CH_2Cl_2–*n*-hexane gave 9-bromo-10-methylphenanthrene (15.03 g, 82% yield). ^1H NMR ($CDCl_3$, 270 MHz) δ 2.95 (s, 3H), 7.61–8.69 (m, 8H) ppm. A CCl_4 (60 mL) solution of 9-bromo-10-methylphenanthrene (16.469 g, 59.634 mmol), *N*-bromosuccinimide (11.147 g, 60.4 mmol), benzoyl peroxide (catalytic amount) was stirred under reflux for 1 h. Float colorless solid was removed by filtration. 10% NaOH aq was added to the filtrate and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from CH_2Cl_2–*n*-hexane gave 9-bromo-10-(bromomethyl)phenanthrene (17.645 g, 83% yield). Yellow solid; ^1H NMR ($CDCl_3$, 270 MHz) δ 5.31 (s, 2H), 7.66-8.74 (m, 8H) ppm. 60% NaH (1.53 g, 38.4 mmol) in oil was washed with distilled hexane and THF (10 mL) was added. To the suspension, THF (50 mL) solution of cinnamyl alcohol (3.43 g, 25.58 mmol) was slowly added under argon atmosphere. The solution was refluxed for 1 h, then cooled to room temperature. THF (60 mL) solution of 9-bromo-10-(bromomethyl)phenanthrene (4.48 g, 12.8 mmol) was slowly added. The solution was refluxed for 2 h, then cooled to room temperature. H_2O and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the residue by column chromatography on silica gel (eluent; *n*-hexane : CH_2Cl_2 = 1 : 1) followed by recrystallization from CH_2Cl_2–*n*-hexane gave

9-bromo-10-phenanthrylmethyl *trans*-3′-phenyl-2′-propenyl ether (2.73 g, 53% yield). Colorless solid; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.35 (d, J = 6.0 Hz, 2H), 5.42 (s, 2H), 6.34–6.40 (m, 1H), 6.66 (d, J = 16.5 Hz, 1H), 7.22–7.40 (m, 5H), 7.66-7.74 (m, 4H), 8.34–8.37 (m, 1H), 8.52–8.56 (m, 1H), 8.67–8.72 (m, 2H) ppm. A mixture of 9-bromo-10-phenanthrylmethyl *trans*-3′-phenyl-2′-propenyl ether (3.09 g, 7.64 mmol), *N*-methylpyrrolidone (9 mL), CuCN (2.05 g, 23.1 mmol) was stirred at 180 °C for 20 min to give black suspension. NH_3 aq (231 mmol) was added at room temperature and the mixture was filtered by suction filtration with CH_2Cl_2. H_2O was added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. *N*-methylpyrrolidone was removed by distillation under reduced pressure. Separation of the black residue by column chromatography on silica gel (eluent; *n*-hexane : CH_2Cl_2 = 1 : 1) followed by recrystallization from CH_2Cl_2–*n*-hexane gave 9-cyano-10-phenanthrylmethyl *trans*-3′-phenyl-2′-propenyl ether (*trans*-**1a**, 1.87 g, 70% yield). Yellow solid; mp 107–108 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.34 (dd, J = 6.1, 1.2 Hz, 2H), 6.34 (dt, J = 15.9, 6.1 Hz, 1H), 6.68 (d, J = 15.9 Hz, 1H), 7.22–7.40 (m, 5H), 7.73–7.82 (m, 4H), 8.33–8.38 (m, 1H), 8.41–8.45 (m, 1H), 8.67–8.74 (m, 2H) ppm; IR (KBr) ν 968, 1114, 1449, 1685, 2221, 2878, 3026 cm^{-1}; MS (EI) m/z 105, 115, 133, 189, 217, 305, 349 (M^+).

4.3. Preparation of 9-cyano-10-phenanthrylmethyl trans-3′-p-cyanophenyl-2′-propenyl ether (trans-**1e**)

To a benzene (100 mL) solution of PPh_3 (5.24 g, 20.0 mmol) was slowly added methyl bromoacetate (3.06 g, 20.0 mmol), and stirred for 10 min. The white suspension was stirred for additional 2 h. The white solid was collected by suction filtration, and washed with benzene (20 mL) twice. The solid was dried under reduced pressure, and then dissolved in deionized water in saturated concentration. Phenolphthalein solution (1 drop) was added and 2 M NaOH aq was slowly added to give white solid until the color turned to pale pink. The solid was collected by suction filtration and washed with deionized water (30 mL) twice. The white solid was dried under reduced pressure for 2 days to give $Ph_3P{=}CHCO_2Me$ (5.51 g, 83% yield). To a dry CH_2Cl_2 (20 mL) solution of *p*-bromobenzaldehyde (2.78 g, 15.0 mmol) was slowly added CH_2Cl_2 (30 mL) solution of $Ph_3P{=}CHCO_2Me$ (5.51 g, 16.5 mmol) under argon atmosphere at 0 °C, and stirred for 1 h. The solvent was removed in vacuo. Small amount of CH_2Cl_2 was added to the oily residue. Et_2O was added to the stirred solution, and the precipitate was removed. The Et_2O solution was washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (eluent; *n*-hexane : EtOAc = 4 : 1, Rf = 0.65) gave methyl *trans*-3-(*p*-bromophenyl)acrylate (3.60 g, 94% yield). ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.75 (s, 3H), 6.45 (d, J = 15.9 Hz, 1H), 7.31 (m, 2H), 7.42 (m, 2H), 7.57 (d, J = 15.9 Hz, 1H) ppm. To a dry toluene (25 mL) solution of *trans*-3-(*p*-bromophenyl)acrylate (6.82 g, 28.2 mmol) was slowly added *i*-Bu_2AlH (1.5 M toluene solution, 37.6 mL) at −78 °C. The solution was warmed to room temperature and stirred for 3 h. 2 N HCl aq (15 mL) was added. The mixture was shaken, and organic layer was extracted. The aqueous phase was washed with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (eluent; *n*-hexane : EtOAc = 4 : 1, then MeOH) gave *trans*-3-*p*-bromophenyl-2-propen-1-ol (5.89 g, 98% yield). Reaction of the alcohol with NaH and 9-bromo-10-(bromomethyl)phenanthrene was carried out under similar conditions described above to give 9-bromo-10-phenanthrylmethyl *trans*-3′-*p*-bromophenyl-2′-propenyl ether in 45% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.33 (dd, J = 5.8, 1.3 Hz, 2H), 5.42 (s, 2H), 6.37 (dt, J = 15.9, 5.8 Hz, 1H), 6.62 (d, J = 15.9 Hz, 1H), 7.20–7.26 (m, 2H), 7.39–7.42 (m, 2H), 7.64–7.73 (m, 4H), 8.33–8.36 (m, 1H), 8.52–8.55 (m, 1H), 8.67–8.71 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 70.4, 70.5, 121.3, 122.5, 122.7, 122.8, 125.8, 126.5, 126.8, 126.9, 127.4, 127.5, 127.9, 129.4, 129.8, 130.2, 131.2, 131.4, 131.5, 131.9, 135.6 ppm. Reaction of this compound with CuCN (15 equiv) was carried out under similar conditions described above. Purification by column chromatography on silica gel (eluent; *n*-hexane–CH_2Cl_2) gave 9-cyano-10-phenanthrylmethyl *trans*-3′-*p*-cyanophenyl-2′-propenyl ether (*trans*-**1e**) in 26% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.37 (dd, J = 5.8, 1.4 Hz, 2H), 5.38 (s, 2H), 6.42 (dt, J = 15.9, 5.8 Hz, 1H), 6.69 (d, J = 15.9 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.75–7.86 (m, 4H), 8.34–8.38 (m, 1H), 8.42–8.46 (m, 1H), 8.70–8.77 (m, 2H) ppm.

4.4. Preparation of 9-cyano-6-methoxy-10-phenanthrylmethyl trans-3′-p-cyanophenyl-2′-propenyl ether (trans-**1f**)

To a mixture of Mg (3.65 g, 150 mmol) in THF (10 mL) was added THF (50 mL) solution of $PhCH_2Cl$ (12.66 g, 100 mmol) dropwisely for 2 h at 0 °C under argon atmosphere. The solution was warmed to room temperature and stirred for 1.5 h. THF (10 mL) solution of *p*-methoxyacetophenone (11.25 g, 75 mmol) was dropwisely added for 30 min, and the solution was stirred for additional 1 h. Sat NH_4Cl aq was poured into the solution at 0 °C. The organic layer was washed with H_2O then brine, separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. To the yellow residue was added benzene and *p*-TsOH (catalytic amount), and the solution was refluxed by a Dean-Stark apparatus until the production of H_2O ceased. Purification by column chromatography on silica gel gave (*E*)-1-methyl-1-*p*-methoxyphenyl-2-phenylethene (6.36 g, 38% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 3.84 (s, 3H), 6.78 (s, 1H), 6.93 (dd, J = 6.9, 2.3 Hz, 2H), 7.19–7.26 (m, 2H), 7.35–7.37 (m, 3H), 7.46–7.49 (m, 2H) ppm. A benzene (200 mL) solution of (*E*)-1-methyl-1-*p*-methoxyphenyl-2-phenylethene (2.5 g, 11.2 mmol) and I_2 (catalytic amount) was bubbled with O_2. The vessel was sealed, and irradiated by 300 W high pressure mercury lamp for 3 days. 10% $Na_2S_2O_3$ aq (100 mL) was added and shaken. The organic layer was washed with H_2O, separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (eluent; *n*-hexane : benzene = 3 : 1, Rf = 0.72) followed by recycling preparative HPLC (GPC, eluent; $CHCl_3$) gave 3-methoxy-10-methylphenanthrene (1.45 g, 59% yield). Mp 55.5–56.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (s, 3H), 4.03 (s, 3H), 7.30 (dd, J = 9.0, 2.5 Hz, 1H), 7.45 (s, 1H), 7.54–7.57 (m, 2H), 7.77–7.80 (m, 1H), 8.00 (d, J = 9.1 Hz, 1H), 8.10 (d, J = 2.7 Hz, 1H), 8.55–8.60 (m, 1H) ppm. A CCl_4 (5 mL) solution of 3-methoxy-10-methylphenanthrene (36.5 mg, 0.164 mmol) was added CCl_4 (10 mL) solution of Br_2 (23.6 mg, 0.148 mmol) at −10 °C, and stirred for 30 min. After the solution was warmed to room temperature, 10% NaOH aq (5 mL) was added. The organic layer was washed with H_2O, separated, dried over Na_2SO_4, filtered, and concentrated in vacuo to give 9-bromo-3-methoxy-10-methylphenanthrene (40.1 mg, 90% yield). Notice! When this reaction was carried out at 0 °C, bromination occurred at 2-position. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.91 (s, 3H), 4.00 (s, 3H), 7.22–7.26 (m, 2H), 7.55–7.67 (m, 2H), 8.00–8.04 (m, 2H), 8.41–8.45 (m, 1H), 8.53–8.56 (m, 1H) ppm. A CCl_4 (10 mL) solution of 9-bromo-3-methoxy-10-methylphenanthrene (0.05 g, 0.166 mmol), *N*-bromosuccinimide (0.0295 g, 0.166 mmol), benzoyl peroxide (catalytic amount) was stirred under reflux for 40 min. Float colorless solid was removed by filtration. 10% NaOH aq was added to the filtrate and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Recrystallization from CH_2Cl_2–*n*-hexane gave 9-bromo-10-bromomethyl-3-methoxyphenanthrene (57 mg, 89% yield). Colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.03 (s, 3H), 5.26 (s, 2H), 7.32–7.36 (m, 1H), 7.66–7.70

(m, 2H), 8.05–8.06 (m, 1H), 8.13 (d, J = 9.1 Hz, 1H), 8.45–8.49 (m, 1H), 8.55–8.58 (m, 1H) ppm. Reaction of this compound (0.90 g, 2.37 mmol) with *trans*-3-*p*-bromophenyl-2-propen-1-ol (1.26 g, 5.92 mmol) was carried out under similar conditions described above, by using 60% NaH (0.24 g, 5.92 mmol) and dry THF (40 mL). Purification by column chromatography on silica gel (eluent; benzene : *n*-hexane = 1 : 1, Rf = 0.5) gave 9-bromo-3-methoxy-10-phenanthrylmethyl *trans*-3′-*p*-bromophenyl-2′-propenyl ether (0.78 g, 64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.02 (s, 3H), 4.30 (dd, J = 6.1, 1.4 Hz, 2H), 5.38 (s, 2H), 6.36 (dt, J = 15.9, 6.1 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 7.19–7.42 (m, 5H), 7.66–7.70 (m, 2H), 8.04 (m, 1H), 8.27 (d, J = 9.0 Hz, 1H), 8.49–8.52 (m, 1H), 8.57–8.60 (m, 1H) ppm. Reaction of this compound with CuCN was carried out under similar conditions described above to give 9-cyano-6-methoxy-10-phenanthrylmethyl *trans*-3′-*p*-cyanophenyl-2′-propenyl ether (*trans*-**1f**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.06 (s, 3H), 4.35 (dd, J = 5.6, 1.5 Hz, 2H), 5.34 (s, 2H), 6.41 (dt, J = 15.9, 5.8 Hz, 1H), 6.68 (d, J = 15.9 Hz, 1H), 7.36 (dd, J = 9.1, 2.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.55–7.59 (m, 2H), 7.72–7.79 (m, 2H), 8.07 (d, J = 2.4 Hz, 1H), 8.30–8.39 (m, 2H), 8.61–8.65 (m, 1H) ppm.

4.5. Preparation of other substrates

Other substrates were prepared by similar methods described above. Data for 9-phenanthrylmethyl *trans*-3′-phenyl-2′-propenyl ether (*trans*-**1c**); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.32 (dd, J = 6.0, 1.5 Hz, 2H), 5.08 (s, 2H), 6.39 (dt, J = 16.4, 6.0 Hz, 1H), 6.68 (d, J = 16.4 Hz, 1H), 7.23–7.42 (m, 5H), 7.58–7.69 (m, 4H), 7.81 (s, 1H), 7.86–7.91 (m, 1H), 8.18–8.23 (m, 1H), 8.66–8.76 (m, 2H) ppm. Data for 9-cyano-10-phenanthrylmethyl *trans*-3′-*p*-methoxyphenyl-2′-propenyl ether (*trans*-**1d**). ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.80 (s, 3H), 4.33 (dd, J = 6.4, 0.9 Hz, 2H), 5.35 (s, 2H), 6.21 (dt, J = 15.9, 6.4 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.82–6.87 (m, 2H), 7.29–7.35 (m, 2H), 7.71–7.84 (m, 4H), 8.34–8.38 (m, 1H), 8.44 (dd, J = 8.1, 1.5 Hz, 1H), 8.70–8.75 (m, 2H) ppm.

4.6. General procedure for photoreaction

In preparative photoreaction, a dry benzene (200 mL) solution containing *trans*-**1** (1 mmol, 5 mM) was placed in cylindrical Pyrex vessels (ϕ = 8 mm). In experiments listed in Table 1, *trans*-**1** (0.03 mmol) in benzene-d_6 (0.6 mL) was placed in an NMR test tube (ϕ = 5 mm). The solution was degassed by argon bubbling for 15 min and then the vessel was sealed. The solution was irradiated by using a 300 W high pressure mercury lamp (Eikosha, PIH-300) at room temperature (> 280 nm light). The temperature of the solution was kept around room temperature by circulated cooling water during irradiation. Data for *r*-3a,*t*-4,*c*-4a,*t*-12b-4-phenyl-3,3a,4,4a-tetrahydro-1*H*-phenanthro[9′,10′:1,4]cyclobuta[1,2-*c*]furan-4a-carbonitrile (**2a**); colorless solid; mp 183–184 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.21–3.26 (m, 1H), 3.96–4.10 (m, 2H), 4.21 (d, J = 6.9 Hz, 1H), 4.47 (d, J = 11.0 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.83–6.89 (m, 3H), 7.05–7.21 (m, 4H), 7.36–7.45 (m, 3H), 7.89 (d, J = 8.2 Hz, 1H), 7.94–8.01 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.6, 49.6, 55.6, 57.4, 74.0, 79.1, 121.9, 122.6, 123.4, 125.7, 127.4, 127.6, 127.9, 127.9, 128.1, 128.5, 128.9, 129.0, 130.6, 131.0, 131.2, 133.6, 136.2 ppm; IR (KBr) ν 909, 1073, 1447, 1489, 2231, 2868 cm^{-1}; MS (EI) m/z 105, 115, 133, 189, 217, 305, 349 (M^+). Data for *trans*-(*Z*)-13-phenyl-1,3,13,13a-tetrahydrodibenzo[4,5:6,7]cycloocta[1,2-*c*]furan-4-carbonitrile (**3a**). Colorless solid; mp 179 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23–3.30 (m, 1H), 3.74 (dd, J = 8.9, 5.1 Hz, 1H), 3.88 (dd, J = 8.9, 2.1 Hz, 1H), 4.20 (d, J = 9.6 Hz, 1H), 4.69 (s, 2H), 6.96–7.51 (m, 13H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 50.6, 55.0, 70.8, 73.2, 105.7, 116.2, 126.5, 126.5, 126.6, 127.5, 127.6, 128.0, 128.6, 129.2, 130.9, 131.7, 133.4, 133.6, 138.4, 140.6, 142.3, 143.6, 165.1 ppm; IR (KBr) ν 1064, 1438, 1483, 2213, 2875 cm^{-1}.

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References

[1] J.J. McCullough, Chem. Rev. 87 (1987) 811–860.
[2] D. De Keukeleire, S.-L. He, Chem. Rev. 93 (1993) 359–380.
[3] J. Cornelisse, Chem. Rev. 93 (1993) 615–669.
[4] T. Miyamoto, T. Mori, Y. Odaira, Chem. Commun. (1970) 1598–1598.
[5] G. Kaupp, Angew. Chem. Int. Ed. Engl. 12 (1973) 765–767.
[6] R.A. Caldwell, J. Am. Chem. Soc. 95 (1973) 1690–1692.
[7] K. Mizuno, C. Pac, H. Sakurai, J. Am. Chem. Soc. 96 (1974) 2993–2994.
[8] R.A. Caldwell, L. Smith, J. Am. Chem. Soc. 96 (1974) 2994–2996.
[9] D. Creed, R.A. Caldwell, J. Am. Chem. Soc. 96 (1974) 7369–7371.
[10] S. Farid, S.E. Hartman, J.C. Doty, J.L.R. Williams, J. Am. Chem. Soc. 97 (1975) 3697–3702.
[11] R.A. Caldwell, N.I. Ghali, C.-K. Chien, D. DeMarco, L. Smith, J. Am. Chem. Soc. 100 (1978) 2857–2863.
[12] D. Creed, R.A. Caldwell, M.M. Ulrich, J. Am. Chem. Soc. 100 (1978) 5831–5841.
[13] R.A. Caldwell, D. Creed, D.C. DeMarco, L.A. Melton, H. Ohta, P.H. Wine, J. Am. Chem. Soc. 102 (1980) 2369–2377.
[14] R.A. Caldwell, D. Creed, Acc. Chem. Res. 13 (1980) 45–50.
[15] R.A. Caldwell, K. Mizuno, P.E. Hansen, L.P. Vo, M. Frentrup, C.D. Ho, J. Am. Chem. Soc. 103 (1981) 7263–7269.
[16] F.D. Lewis, S.V. Barancyk, E.L. Burch, J. Am. Chem. Soc. 114 (1992) 3866–3870.
[17] K. Mizuno, R.A. Caldwell, A. Tachibana, Y. Otsuji, Tetrahedron Lett. 33 (1992) 5779–5782.
[18] Y.L. Chow, S.P. Wu, X. Ouyang, J. Org. Chem. 59 (1994) 421–428.
[19] H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R.A. Caldwell, C.-C. Hsu, J. Am. Chem. Soc. 104 (1982) 6796–6797.
[20] H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R.A. Caldwell, C.-C. Hsu, Bull. Chem. Soc. Jpn. 63 (1990) 1049–1057.
[21] H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R.A. Caldwell, C.-C. Hsu, Bull. Chem. Soc. Jpn. 63 (1990) 1058–1061.
[22] N. Tanaka, H. Yamazaki, H. Sakuragi, K. Tokumaru, Bull. Chem. Soc. Jpn. 67 (1994) 1434–1440.
[23] C. Pac, T. Sugioka, K. Mizuno, H. Sakurai, Bull. Chem. Soc. Jpn. 46 (1973) 238–243.
[24] J.J. McCullough, R.C. Miller, D. Fung, W.-S. Wu, J. Am. Chem. Soc. 97 (1975) 5942–5943.
[25] J.J. McCullough, R.C. Miller, W.-S. Wu, Can. J. Chem. 55 (1977) 2909–2915.
[26] K. Mizuno, C. Pac, H. Sakurai, J. Org. Chem. 42 (1977) 3313–3315.
[27] C. Pac, K. Mizuno, H. Okamoto, H. Sakurai, Synthesis (1978) 589–590.
[28] I.A. Akhtar, J.J. McCullough, J. Org. Chem. 46 (1981) 1447–1450.
[29] Y. Inoue, K. Nishida, K. Ishibe, T. Hakushi, N.J. Turro, Chem. Lett. (1982) 471–474.
[30] H. Suginome, C.F. Liu, M. Tokuda, A. Furusaki, J. Chem. Soc. Perkin Trans. 1 (1985) 327–329.
[31] Y.L. Chow, G.E. Buono-Core, X.-Y. Liu, K. Itoh, P. Qian, J. Chem. Soc. Chem. Commun. (1987) 913–915.
[32] A. Albini, E. Fasani, F. Giavarini, J. Org. Chem. 53 (1988) 5601–5607.
[33] K. Mizuno, K. Nakanishi, M. Yasueda, H. Miyata, Y. Otsuji, Chem. Lett. (1991) 2001–2004.
[34] N. Zupancic, B. Sket, J. Chem. Soc. Perkin Trans. 1 (1992) 179–180.
[35] D. Döpp, A.W. Erian, G. Henkel, Chem. Ber. 126 (1993) 239–242.
[36] H. Weng, H.D. Roth, Tetrahedron Lett. 37 (1996) 4895–4898.
[37] T. Noh, D. Kim, Y.-J. Kim, J. Org. Chem. 63 (1998) 1212–1216.
[38] A. Yokoyama, K. Mizuno, Org. Lett. 2 (2000) 3457–3459.
[39] Y. Kubo, T. Inoue, H. Sakai, J. Am. Chem. Soc. 114 (1992) 7660–7663.
[40] Y. Kubo, K. Kiuchi, I. Inamura, Bull. Chem. Soc. Jpn. 72 (1999) 1101–1108.
[41] Y. Kubo, K. Kusumoto, S. Nakajima, I. Inamura, Chem. Lett (1999) 113–114.
[42] T.R. Chamberlain, J.J. McCullough, Can. J. Chem. 51 (1973) 2578–2589.
[43] K. Mizuno, C. Pac, H. Sakurai, J. Chem. Soc. Perkin Trans. 1 (1975) 2221–2227.
[44] M. Mella, E. Fasani, A. Albini, J. Org. Chem. 57 (1992) 6210–6216.
[45] H. Mukae, H. Maeda, K. Mizuno, Angew. Chem. Int. Ed. 45 (2006) 6558–6560.
[46] H. Maeda, A. Sugimoto, K. Mizuno, Org. Lett. 2 (2000) 3305–3308.
[47] S.L. Murov, I. Carmichael, G.L. Hug (Eds.), Handbook of Photochemistry, Second Edition, Marcel Dekker, Inc., New York, 1993.
[48] R.A. Caldwell, D. Creed, T.-S. Maw, J. Am. Chem. Soc. 101 (1979) 1293–1295.