Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Preparation of polycyclic compounds by intramolecular photospirocyclization and photocycloaddition reactions of 4-alkenyl -1-cyanonaphthalene derivatives

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ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form 6 January 2016
Accepted 7 January 2016
Available online xxx

This paper is dedicated to Prof. Yoshihisa Inoue for his retirement of Osaka University.

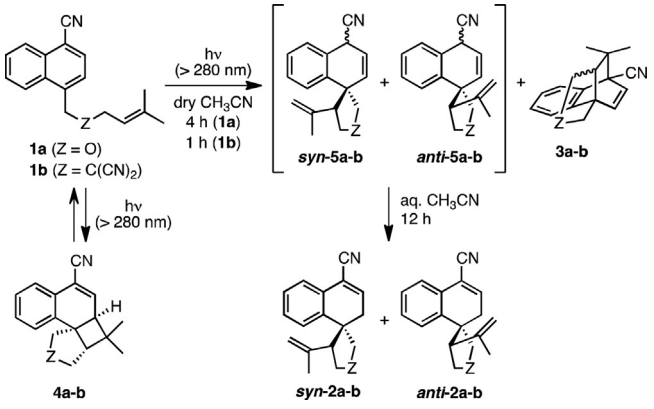
Keywords:
Photoreaction
Spirocyclization
Photocycloaddition
1-Cyano-4-alkenylnaphthalene
Angular triquinane

ABSTRACT

Photoreactions of 4-pentenyl-1-cyanonaphthalenes yield spirocyclic products along with [4+2] cycloadducts. Photoreactions of 5-phenyl derivatives produce a product having tricyclo[6.3.0.0^{1,4}] undecadiene skeleton. Formation of angular triquinanes takes place in photoreactions of cycloalkene-linked cyanonaphthalenes. The observation demonstrates that π–π arene ring interactions, steric hindrance, and suitable locations of reaction sites in *syn* and *anti* singlet exciplexes govern the modes followed in intramolecular photoreactions of 4-alkenyl-1-cyanonaphthalenes.

1. Introduction

Photocycloaddition reactions between alkenes and arenes serve as useful methods for the preparation of polycyclic compounds [1–7]. Although [3+2] photocycloaddition reactions of benzene derivatives with alkenes is a common reaction type, the corresponding reactions of naphthalenes have been much less explored [8–16]. In one study of these processes, we uncovered a high yielding, one-pot method for the synthesis of benzotriquinane derivatives that utilizes intramolecular [3+2] photocycloaddition reactions of 2-alkenyl-1-cyanonaphthalenes [17,18]. The results of this effort showed that intramolecular photocycloadditions have a high potential for use as a general method for the preparation of polycyclic compounds. In continuing studies in this area, we demonstrated that intramolecular photoreactions of 4-alkenyl-1-cyanonaphthalenes can be employed as methods for efficient synthesis of polycyclic compounds, such as spiro[4.5]decadienes, tricyclo[6.3.0.0^{1,4}]undecadienes and angular triquinanes. The results of this effort are described below.



Scheme 1. Photoreaction of **1a-b**.

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http://dx.doi.org/10.1016/j.jphotochem.2016.01.005
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Table 1
Product ratio on photoreaction of **1a-b**.

Substrate	Z	Irradiation time (h)	Product ratio[a] (isolated yields (%))				Conversion (%)
			***syn*-2**	***anti*-2**	**3**	**4**	
1a	O	4	50 (43)	25	25	0	100
1b	$C(CN)_2$	1	50	25	25 (24)	0	100

Conditions: irradiated with a high pressure mercury lamp ([**1a**] = 30 mM, [**1b**] = 3 mM) and then treated with aq. CH_3CN for 12 h.
[a] Determined by ^1H NMR.

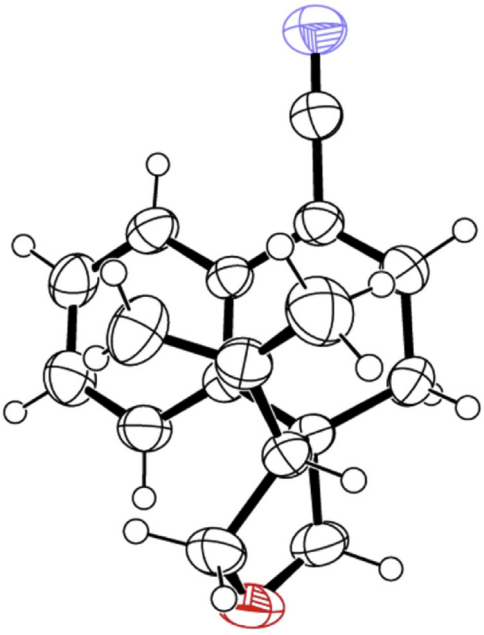
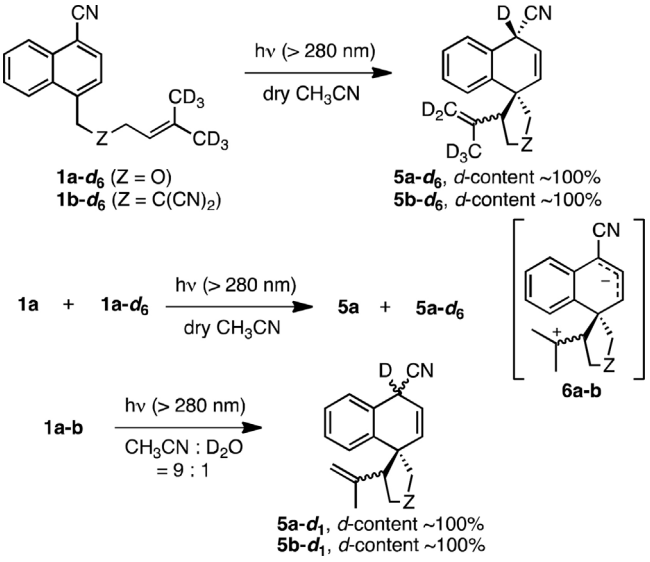


Fig. 1. ORTEP drawing of ***syn*-2a**.



Scheme 2. Experiments to investigate the mechanism.

2. Results and discussion

2.1. Spirocyclization reactions

Dry acetonitrile solutions containing 1-cyanonaphthalene derivatives **1a-b**, containing 4-pentenyl and 2-oxa-4-pentenyl groups at C-4 of the naphthalene ring, in Pyrex vessels (>280 nm) were irradiated using a 300 W high pressure mercury lamp for 4 (**1a**) and 1 h (**1b**) (Scheme 1). The photolysates were diluted with aqueous acetonitrile (CH_3CN:H_2O = 9:1) and let stand for 12 h. The products generated in these reaction sequences were analyzed by using ^1H NMR and separated by using column chromatography on silica gel followed by recycling preparative HPLC. The results show that photoreactions of **1a-b** produce *syn*- and *anti*-spiro[4.5] decadienes **2a-b**, and [4 + 2] cycloadducts **3a-b** in ca. 2:1:1 ratios (Table 1). The main product, ***syn*-2a**, formed by irradiation of **1a** was isolated in 43% yield and demonstrated by using X-ray crystallographic analysis (Fig. 1) to have the assigned structure and a stereochemistry in which the isopropenyl group is located in the *syn* direction relative to the benzene ring. ^1H NMR analysis of the photolysates was utilized to show that ***syn*-** and ***anti*-5a-b** are the

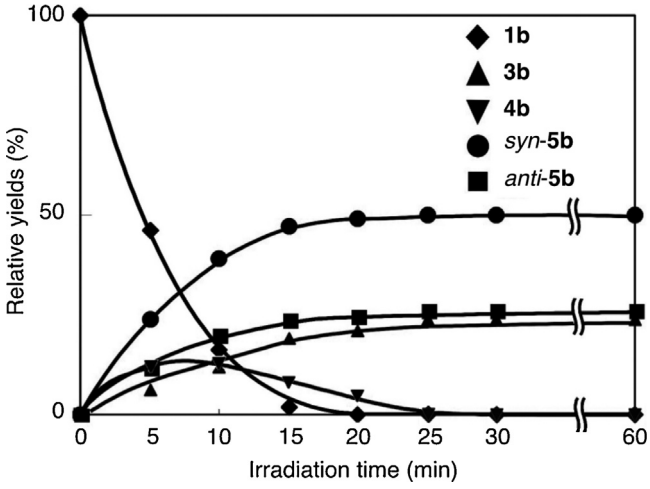
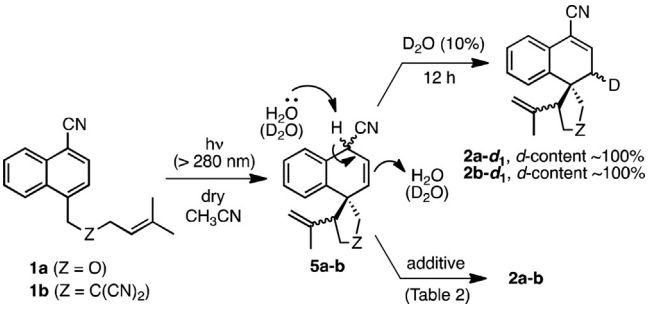


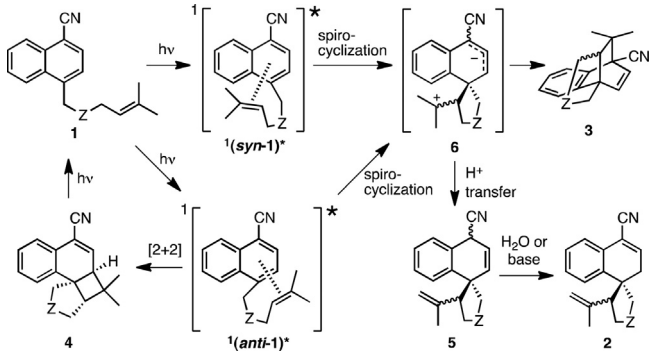
Fig. 2. Time dependency in the photoreaction of **1b** in dry CH_3CN, determined by ^1H NMR.



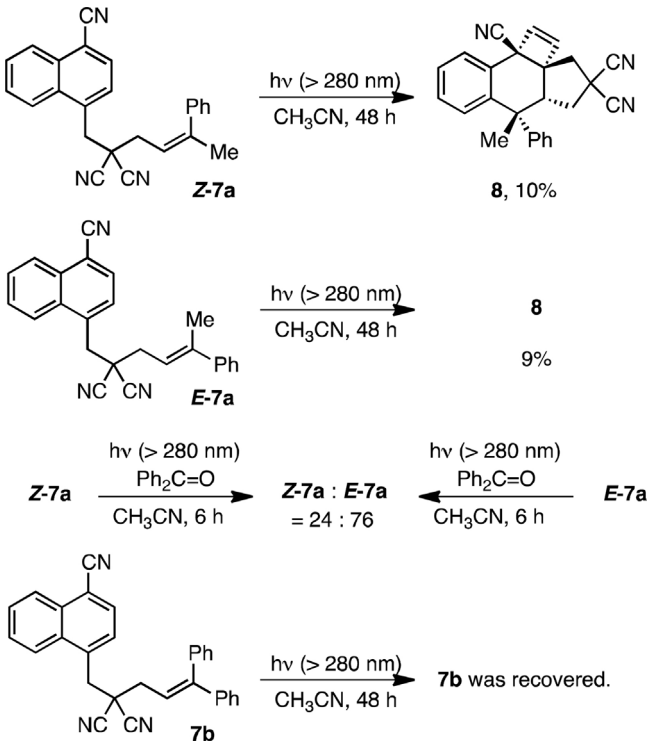
Scheme 3. Isomerization from **5a-b** to **2a-b**.

Table 2
Effect of additives on the isomerization from **5b** to **2b**.

Additive	Time (h)	Conversion (%)
None	12	0
CH_3COOH (5%)	12	0
H_2O (10%)	12	100
Et_3N (5%)	2	100
Pyridine (5%)	2	100



Scheme 4. Proposed mechanism for spirocyclization of **1**.

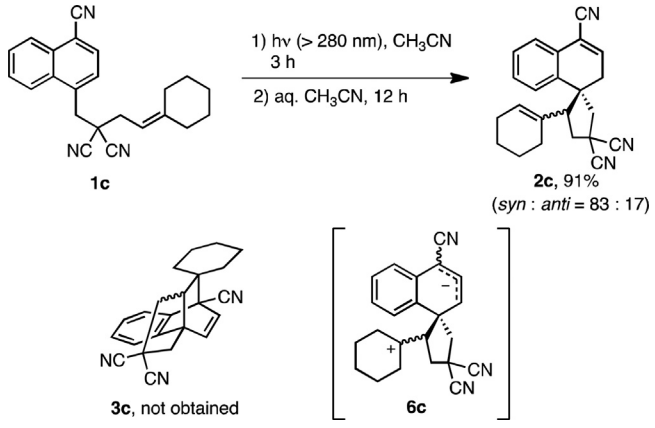


Scheme 6. Photoreactions of **7a-b**.

initially formed photoproducts and that these substances are transformed to the corresponding *syn*- and *anti*-**2a-b** regioisomers upon treatment with aqueous acetonitrile.

The time dependence of the yields of products generated in the photoreaction of **1b** in dry acetonitrile were monitored by using ^{1}H NMR spectroscopy. The results (Fig. 2) show that [2 + 2] photocycloadduct **4b** is produced at the initial stage of the photoreaction and that this substance disappears upon prolonged photoirradiation. Moreover, in concert with the disappearance of **4b** the amounts of ***syn*-5b**,***anti*-5b** and **3b** in a ratio of 2:1:1 increase with increasing irradiation time. The results of monitoring the photoreaction of **1b** in benzene showed that the same trends in product formation and disappearance take place.

Several experiments using deuterium labeled substrates and solvents were carried out to investigate the mechanistic pathways



Scheme 5. Formation of spiro compounds in photoreaction of **1c**.

followed in formation of the spirocyclic products (Scheme 2). Photoreactions of **1a-d_6** and **1b-d_6** in which the terminal methyl groups in each are fully deuteriated, in dry CH_3CN gave **5a-d_6** and **5b-d_6** in which the carbon α to the CN group in each is 100% mono-deuteriated, respectively. Photoreactions of an equimolar mixture of **1a** and **1a-d_6** produced **5a** and **5a-d_6** and none of the crossover products **5a-d_1** and **5a-d_5**. These results show that hydrogen (perhaps proton) transfer from the methyl group in **1a** to the carbon α to CN group occurs intramolecularly (perhaps via of zwitterion intermediate **6a**). Photoreactions of **1a-b** in 9:1CH_3CN:D_2O produced **5a-d_1** and **5b-d_1** in which the carbon α to the CN group in each is 100% mono-deuteriated. This result suggests that D_2O can mediate what must be an intramolecular proton transfer process.

In another experiment, the photolysates, containing **5a-b**, produced by photoreactions of **1a-b** in dry CH_3CN were treated with D_2O (10% vs CH_3CN) (Scheme 3) and let stand for 12 h. Analysis of the product mixtures showed that **2a-d_1** and **2b-d_1** having deuterium at the allylic positions, are generated in this process. In order to clarify the role played by water, the effect of additives on the isomerization reaction of **5b** to form **2b** was studied (Table 2). The results show that the isomerization did not occur when acetic acid (5%) was added and that addition of Et_3N (5%) or pyridine (5%) promotes the isomerization reaction. These findings indicate that water acts as a base to abstract α-protons in the isomerization reactions of **5a-b** to form the more stable **2a-b**.

The results described above enable formulation of the possible mechanism for spirocyclization reactions of **1a-b** shown in Scheme 4. In the first step of this route, both *syn* ^{1}(***syn*-1**)* and *anti* ^{1}(***anti*-1**)* singlet exciplexes are generated between the singlet excited state of the cyanonaphthalene chromophore serving as an electron acceptor and the side chain alkene group serving as an electron donor. ^{1}(***Anti*-1**)* can serve as a precursor for the

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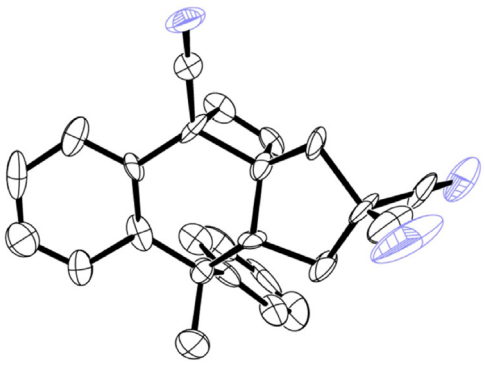


Fig. 3. ORTEP drawing of **8**.

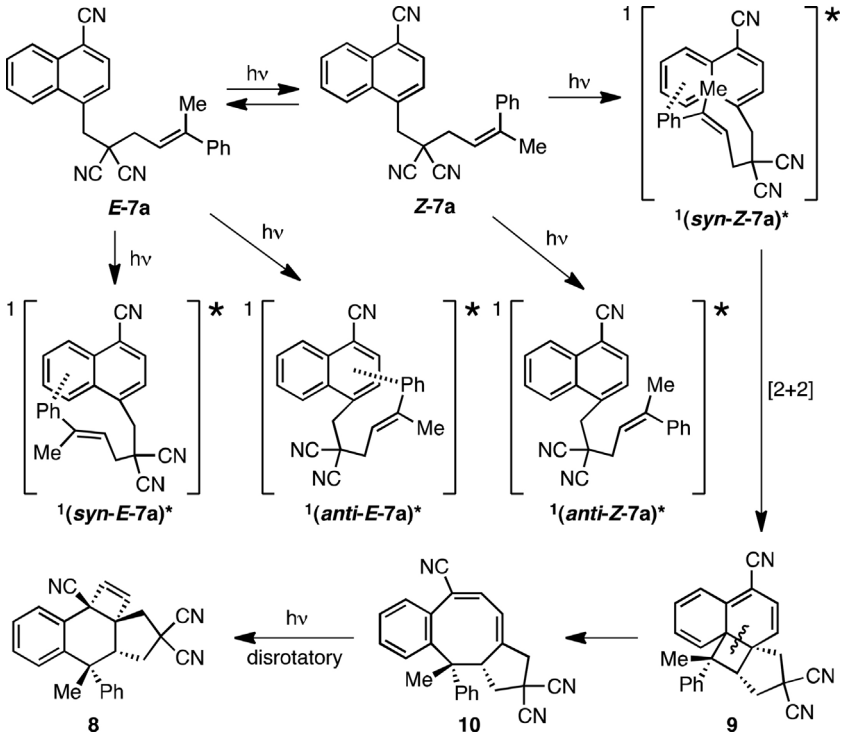
reversibly formed [2+2] photocycloadduct **4**. Spirocyclization reactions of both ^{1}(***syn*-1**)* and ^{1}(***anti*-1**)* generate *syn* and *anti* zwitterionic intermediates **6**, which can undergo C—C bond formation to produce [4+2] cycloadducts **3**. Alternatively, intramolecular proton transfer in **6** forms the primary photoproducts **5** which undergo base promoted isomerization to give the final spirocyclic products **2**.

With the aim of increasing the selectivity of photoproduct formation, photoreaction of the cyclohexylidene derivative **1c** was performed (Scheme 5). The reaction was found to generate the spirocyclic product **2c** exclusively in a 91% yield and a 83:17 *syn*:*anti* ratio. The increase of chemoselectivity seen in this process might be consequence of steric hindrance provided by the cyclohexylidene group in the zwitterionic intermediate **6c**, which prevents formation of the [4+2] cycloadduct **3**.

2.2. Formation of tricyclo[6.3.0.0^{1,4}]undecadienes

Photoreaction of ***Z*-7a**, possessing a phenyl group at the terminal position of the alkene moiety, in CH_3CN for 48 h gave oligomeric products as a result of the presence of the styrene moiety (Scheme 6). The sole isolable monomeric product (10%) produced in this process was a single stereoisomer of the tricyclo[6.3.0.0^{1,4}]undecadiene **8**. The structure and stereochemistry of **8** were assigned using X-ray crystallographic analysis (Fig. 3). Interestingly, photoreaction of ***E*-7a** led to production of **8** in 9% yield. This observation suggests that *E*/*Z* isomerization takes place under the photoreaction conditions to generate a mixture of ***Z*-7a** and ***E*-7a**. Indeed, individual benzophenone triplet sensitized [19] photoreactions of ***Z*-7a** and ***E*-7a** for 6 h were found to promote *E*/*Z* photoisomerization to give in each case a 24:76 mixture of ***Z*-7a** and ***E*-7a**. Finally, the diphenyl derivative **7b** was observed to be unreactive even when irradiated for long time periods.

The mechanism proposed for photoreactions of ***E*-7a** and ***Z*-7a** is shown in Scheme 7. In the route, photoexcitation of both ***E*-7a** and ***Z*-7a** leads to formation of the *syn* and *anti* singlet exciplexes ^{1}(***syn*-*E*-7a)***, ^{1}(***anti*-*E*-7a)***, ^{1}(***anti*-*Z*-7a)*** and ^{1}(***syn*-*Z*-7a)***. The structure of **8** suggests that among the four possible exciplexes ^{1}(***syn*-*Z*-7a)***, in which π–π interactions occur between the phenyl group and naphthalene ring, is the likely intermediate involved in formation of [2+2] cycloadduct **9**, which is the primary photoproduct. Thermally induced disrotatory, 6π electrocyclic ring opening of **9** then gives **10**, which undergoes secondary photochemical, disrotatory 4π ring closure to form **8**. A possible reason why the diphenyl derivative **7b** does not follow this reaction pathway may be steric hindrance which blocks operation of the



Scheme 7. Proposed mechanism for the formation of tricyclo[6.3.0.0^{1,4}]undecadiene **8**.

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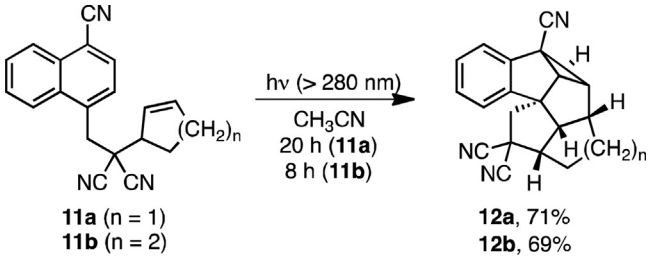


Scheme 8. Photoreaction of **11a-b**.

initial [2 + 2] photocycloaddition step, only photoinduced *cis–trans* isomerization may take place.

2.3. Formation of angular triquinanes

It was anticipated that photoreactions of cycloalkene linked cyanonaphthalenes would produce angular triquinanes, whose basic skeleton is found in natural products contained in plants [20,21]. Indeed, irradiation of acetonitrile solutions of cyanonaphthalenes **11a-b** produced triquinanes **12a** and **12b** as single stereoisomers in 71% and 69% respective isolated yields (Scheme 8). The structure and stereochemistry of these substances were assigned by using X-ray crystallographic analysis (Fig. 4). Importantly, spirocyclic and tricyclo[6.3.0.0^{1,4}]undecadiene products are not produced in these processes.

A likely mechanism for the high yielding formation of the angular triquinanes is shown in Scheme 9. The singlet excited state of **11** can form both *syn* and *anti* exciplexes, ^{1}(***syn*-11**)* and ^{1}(***anti*-11**)*. The former exciplex is unable to undergo spirocyclization or [2 + 2] photocycloaddition because of steric hinderance or some structural reason. In contrast, the *anti*-type exciplexes ^{1}(***anti*-11**)* can adopt a conformation that can undergo intramolecular [3 + 2] photocycloaddition at the 2,4-positions of the naphthalene ring to give the tertially benzylic α-CN containing biradical **13**. It should be noted that the orientation of the cycloalkene ring in ^{1}(***anti*-11**)* is favorable for the biradical forming cycloaddition process. The intramolecular bonding between the radical centers in biradical **13** then forms the angular triquinane **12**.

2.4. Discussion

Inspection of the UV–vis absorption spectra of the alkene linked cyanonaphthalenes in CH_2Cl_2 (1×10^{-4} M) (Figs. 5 and 6) were found

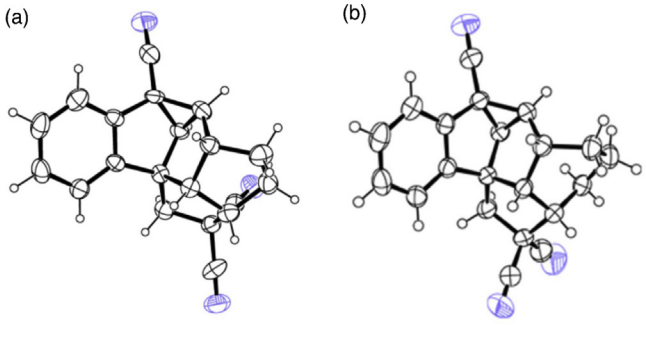
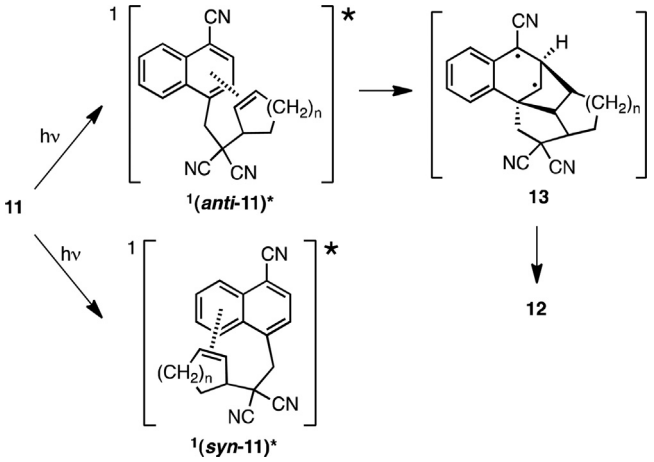


Fig. 4. ORTEP drawings of (a) **12a** and (b) **12b**.



Scheme 9. Proposed mechanism for the formation of angular triquinanes **12**.

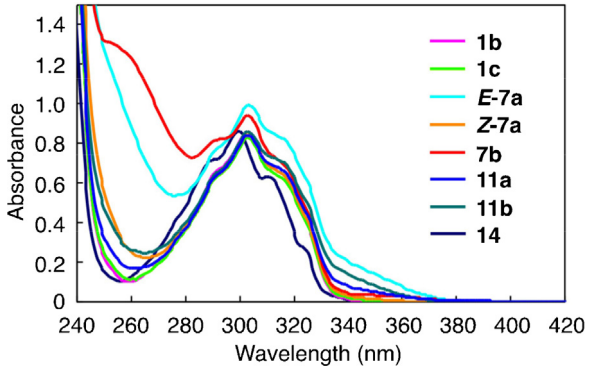
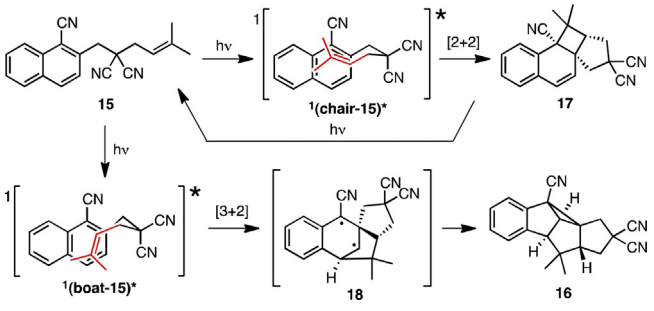


Fig. 5. UV–vis absorption spectra of substrates in this study and 1-cyano-4-methylnaphthalene (**14**) in aerated CH_2Cl_2 (1.0×10^{-4} M).

to have absorption bands in the range of 260–360 nm attributable to π–π* transitions of 1-cyanonaphthalene chromophore and absorption maxima at 301–305 nm ($\varepsilon = 8.2 \times 10^3$–$9.8 \times 10^3$ mol^{-1} dm^3 cm^{-1}). These observations show that by using >280 nm light the 1-cyanonaphthalene moiety is excited exclusively. Fluorescence



Scheme 10. Photoreaction of 1-cyano-2-alkenylnaphthalene (Ref. [17]).

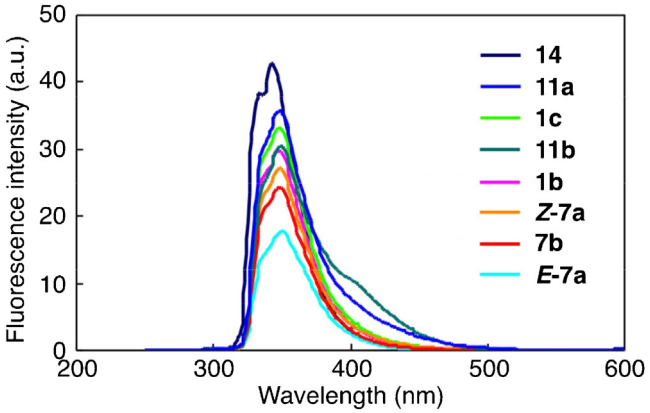
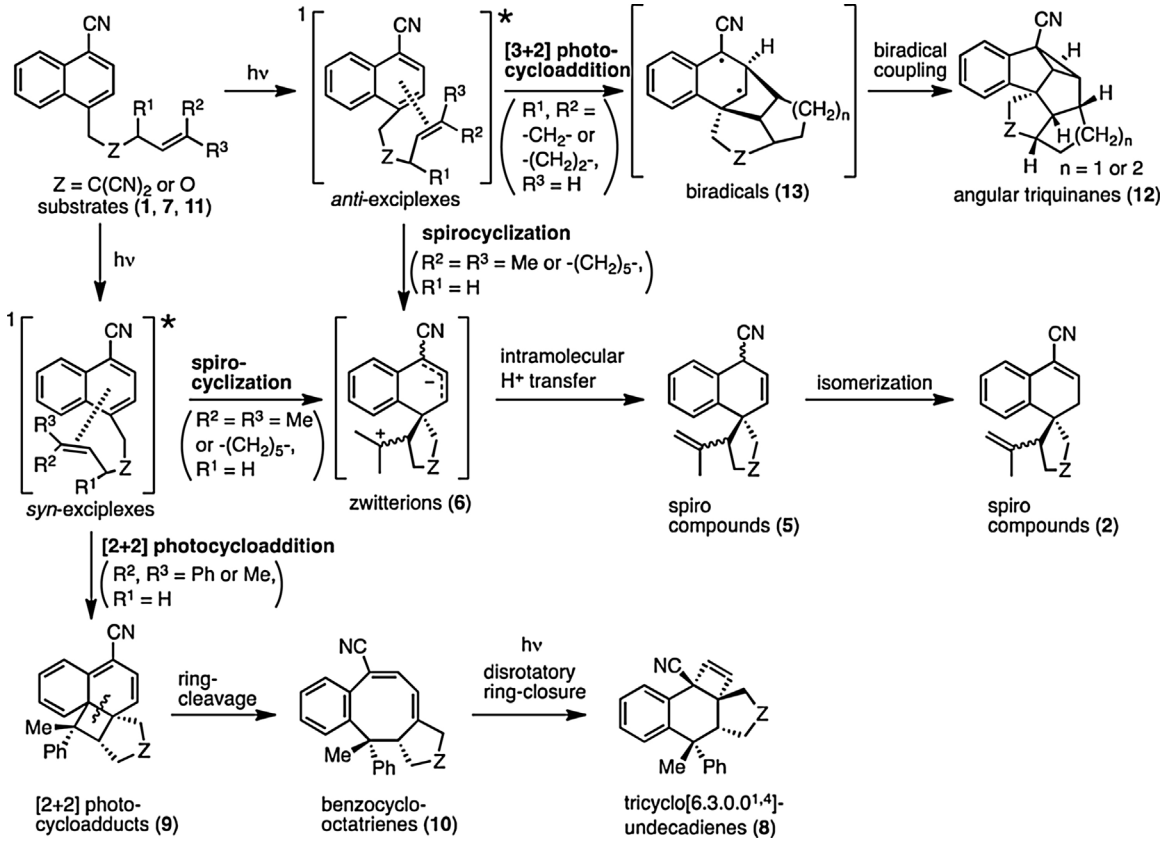


Fig. 6. Fluorescence spectra of substrates in this study and 1-cyano-4-methylnaphthalene (**14**) in aerated CH_2Cl_2 (excited at absorption maxima, fluorescence intensity was adjusted to the absorbance at absorption maxima).

spectra of these substances (ca. 1×10^{-4} M in aerated CH_2Cl_2) contain maxima associated with monomer emission from the 1-cyanonaphthalene fluorophore that is partially quenched by the internal alkene moiety. The fluorescence efficiencies were found to decrease in the order of 1-cyano-4-methylnaphthalene (**14**) > **11a** > **1c** > **11b** > **1b** > ***Z*-7a** > **7b** > ***E*-7a**, phenomena again associated with increasing intramolecular fluorescence quenching. Typical exciplex emission was observed for **11b** at 400 nm maximum and weak exciplex emission was also observed for **11a** at a longer wavelength (380–500 nm).

The results of many studies show that photocycloaddition reactions of arenes with alkenes are synthetically useful processes [1–7]. Moreover, it has been found that photoreactions of benzenes with alkenes proceed mainly by [2 + 2](*ortho*) and [3 + 2](*meta*) cycloaddition pathways, and to a lesser extent by [4 + 2](*para*) cycloaddition modes. In photoreactions of naphthalenes with alkenes, [2 + 2] cycloaddition at the 1,2-positions of the naphthalene ring is the most common process taking place [22–53]. However, [2 + 2] cycloaddition at the 1,8a-positions [54–56], [3 + 2] cycloaddition at the 1,3-positions [8–11] [3 + 2] cycloaddition at the 1,8-positions [12–16] and [4 + 2] [57–62] photocycloadditions rarely occur.

McCullough et al. reported that intramolecular photoreactions of 1-cyano-2-oxaalkenylnaphthalenes give 1,2-[2 + 2] photocycloadducts [63,64]. In addition, in an earlier effort, we investigated intramolecular photoreactions of the related compounds shown in Scheme 10 [17]. In that study, we observed that photocycloadduct **17** forms exclusively in the initial stage of the photoreaction of **15**, but that the linear triquinane **16** is the main product (74% yield) when irradiation is conducted for a prolonged time period (10 h). This finding was explained by taking into account that **17** can be reversibly photocleaved to form **15** while **16** is unreactive because it does not absorb light at wavelengths >280 nm. Of the two possible singlet exciplexes, ^{1}**(chair-15)*** and ^{1}**(boat-15)***, formed in the initial chemical step of this process, ^{1}**(chair-15)*** appears to be more thermodynamically favorable. A driving force for this uncommon [3 + 2] photocycloaddition process is the extra



Scheme 11. Summary of photoreaction pathways.

stabilization of **18** provided by the presence of tertiary benzylic α-CN radical center. It is important to note that the linear triquinane skeleton is also found in naturally occurring substances [65,66]. In an additional investigation, McCullough found that photoreactions of 1-cyano-4-alkenylnaphthalenes form intramolecular [2+2] photocycloadducts at the 3,4-positions of the naphthalene ring along with unidentified minor products [63,64].

The three types of photoreactions uncovered in this study are summarized in Scheme 11. In these processes, both *syn*-type and *anti*-type singlet exciplexes are likely formed from naphthalene ring centered singlet excited states. Because each face of alkene group can be oriented closer to naphthalene ring in these exciplexes, these complexes have diastereomeric relationships. When R^1 and R^2 in the alkene chain are cyclic and R^3 = H, [3+2] photocycloaddition reaction of the *anti*-exciplex to give biradicals **13** is energetically preferred because of steric reasons. Intramolecular biradical coupling then affords the angular triquinane **12**. On the other hand, when R^2 and R^3 are part of acyclic alkyl groups, both *syn* and *anti*-type exciplexes have similar energies. In these cases the reaction follows a stepwise route producing zwitterionic intermediates **6**. Intramolecular proton transfer in **6** followed by isomerization gives the spirocyclic product **2**. When R^2 or R^3 is a phenyl group, *syn*-type exciplexes are preferentially produced because of the intervention of stabilizing π–π interactions between the phenyl and naphthyl ring. In this case, intramolecular [2+2] photocycloaddition reaction takes place to yield **9**. Ring cleavage of **9** followed by photochemical disrotatory ring closure then produces the tricyclo[6.3.0.0^{1,4}]undecadiene derivative **8**.

Non-exciplex mechanism such as photoinduced electron-transfer (PET) [67–70] seems unlikely because ΔG for PET process calculated by Rehm–Weller equation ($\Delta G = E^{Ox}(D) - E^{red}(A) - E_{0-0} - e^2/\varepsilon r$) [71] is positive in the photoreaction of trisubstituted aliphatic alkenes or cycloalkenes (E^{red} (1-cyanonaphthalene) = −2.33 V vs Ag/Ag$^+$ [67], E^{Ox} (2-methyl-2-butene) = 1.47 V vs Ag/Ag$^+$ [72], E^{Ox} (cyclopentene) = 2.19 V vs SCE [73], E^{Ox} (cyclohexene) = 2.31 V vs SCE [68], E_{0-0} (1-cyanonaphthalene) = 89.4 kcal/mol [67]). However, oxidation potentials of phenyl-substituted alkenes are lower (E^{Ox} (α-methylstyrene) = 1.86 V vs SCE [74], E^{Ox} (1,1-diphenylethylene) = 1.22 V vs SCE [73]) and calculated ΔG becomes negative, therefore PET mechanism in the photoreaction of **7a-b** may be partially involved, but it might not be a major pathway in photoreaction in nonpolar solvent such as benzene.

3. Conclusion

Photoirradiation of acetonitrile solutions containing dimethyl-substituted alkene linked naphthalenes **1** followed by treatment of the photolysate with aqueous CH_3CN gives rise to formation of spiro[4.5]decadiene derivatives **2** in 75% yield and a *syn*:*anti* diastereomer ratio of 67:33. The results of experiments using a D_2O containing solvent and a per-deuteriated substrate demonstrate that formation of **2** follows a mechanistic route in which intramolecular proton transfer occurs in a zwitterionic intermediate. On the other hand, photoreactions of stereoisomeric phenyl-substituted derivatives ***Z*-7a** and ***E*-7a** produce the same product, tricyclo[6.3.0.0^{1,4}]undecadiene **8**, whose structure was determined by using X-ray crystallographic methods. Triplet sensitized photoreactions of ***Z*-7a** and ***E*-7a** gave a photostationary state mixture of ***Z*-7a** and ***E*-7a** in a 24:76 ratio. These results suggest that [2+2] photocycloaddition at the 4,4a-positions of the naphthalene ring takes place to form **8** through a pathway involving *E*–*Z* photoisomerization, formation of a singlet exciplex that has π–π overlap between the arene rings, and thermal ring opening followed by disrotatory ring closure. Cycloalkene linked cyano-naphthalenes **11a-b** undergo photoreactions to generate angular-triquinanes **12a-b** in high yields through a route involving intramolecular [3+2] photocycloaddition. Finally, it is possible to conclude that π–π arene ring interactions, steric hindrance, and suitable locations of reaction sites in *syn* and *anti* singlet exciplexes govern the modes followed in intramolecular photoreactions of 4-alkenyl-1-cyanonaphthalenes.

4. Experimental

4.1. Materials and equipment

Acetonitrile was distilled from CaH_2 and then from P_2O_5. Benzene was distilled from CaH_2 and then from Na. ^{1}H and ^{13}C NMR spectra were recorded using a Varian MERCURY-300 (300 MHz and 75 MHz, respectively) spectrometer 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 Jasco V-530 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-2086 Plus, RI-2031 Plus differential refractometer, Megapak GEL 201C columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted by using Kanto-Chemical Co., Ltd., silica gel 60 N (spherical, neutral, 0.063–0.200 mm). X-ray crystallographic data for a single crystals were obtained using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (SIR92) and expanded by using Fourier techniques. All calculations were performed using the Crystal Structure crystallographic software package.

4.2. General procedure for photoreaction

A dry acetonitrile solution containing substrate (10–30 mM) was placed in a cylindrical Pyrex vessel (ϕ = 8 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. The temperature of the solution was kept around room temperature by circulated cooling water during irradiation.

4.3. Preparation of *1a*

A mixture of 1-methylnaphthalene (8.00 g, 56.3 mmol), Fe powder (cat), I_2 (cat), CCl_4 (25 mL) was stirred and cooled to 0 °C. CCl_4 (5 mL) solution of Br_2 (9.01 g, 2.91 mL, 56.3 mmol) was slowly added and stirred for 2 h. The organic phase was shaken with sat. $Na_2S_2O_3$ aq, 10% NaOH aq, and sat. NaCl aq. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The product, 1-bromo-4-methylnaphthalene (11.8 g, 53.2 mmol, 94% yield) was used without purification. A mixture of 1-bromo-4-methylnaphthalene (11.8 g, 53.2 mmol), CuCN (11.8 g, 131.6 mmol), *N*-methyl-2-pyrrolidone (70 mL) was heated to 200 °C by an oil bath and stirred for 30 min. After cooling to room temperature, 10% NH_3 aq and $CHCl_3$ was added and shaken. The organic layer was concentrated in vacuo to give brown solid. Separation by column chromatography on silica gel (eluent; hexane–AcOEt) gave 1-cyano-4-methylnaphthalene (8.77 g, 52.5 mmol, 99% yield). Colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.77 (s, 3H), 7.36–8.27 (m, 6H) ppm. A CCl_4 (60 mL) solution of 1-cyano-4-methylnaphthalene (7.77 g, 46.5 mmol), *N*-bromosuccinimide (8.28 g, 46.5 mmol), benzoyl peroxide (cat) was refluxed for 3 h. Solid was removed by filtration, and solvent was removed in vacuo. The product, 1-cyano-4-(bromomethyl)naphthalene (10.9 g, 44.5 mmol, 96%

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yield) was used without purification. Yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.93 (s, 2H), 7.59–8.33 (m, 6H) ppm. To THF (10 mL) solution of NaH (0.780 g, 19.5 mmol) was added 3-methyl-2-buten-1-ol (1.29 g, 15.0 mmol) under argon atmosphere. The solution was refluxed for 30 min. THF (100 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (3.69 g, 15.0 mmol) was added at 0 °C and stirred for 1 h. Then it was warmed to room temperature, and stirred for 1 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 1-cyano-4-(5-methyl-2-oxa-4-hexenyl)naphthalene (**1a**, 2.29 g, 9.12 mmol, 61% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 3H), 1.78 (s, 3H), 4.13 (d, J = 6.9 Hz, 2H), 4.98 (s, 2H), 5.44 (m, 1H), 7.62–8.29 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.5, 26.2, 67.4, 69.7, 110.2, 117.9, 120.5, 124.4, 124.5, 125.8, 127.6, 128.2, 131.0, 132.2, 132.4, 138.0, 140.3 ppm; GC–MS (EI) m/z (%) = 251 (9, M^+), 166 (62, $C_{12}H_8N$), 85 (100, C_5H_9).

4.4. Preparation of **1b**

To a mixture of THF (10 mL) and NaH (1.00 g, 25.0 mmol) was added malononitrile (1.50 g, 22.7 mmol) at −78 °C under argon atmosphere, and stirred for 10 min. The solution was warmed to room temperature, 4-bromo-2-methyl-2-butene (5.07 g, 34.0 mmol) was slowly added, and stirred for 30 min. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 5,5-dicyano-2-methyl-2-pentene (2.10 g, 15.7 mmol, 69%). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73 (s, 3H), 1.80 (s, 3H), 2.73 (dd, J = 6.6, 1.3 Hz, 2H), 3.67 (t, J = 6.6 Hz, 1H), 5.22 (t, J = 1.3 Hz, 1H) ppm. To THF (5 mL) solution of NaH (0.400 g, 10.0 mmol) was added 5,5-dicyano-2-methyl-2-pentene (0.580 g, 4.33 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (100 mL) solution of 1-cyano-4-(bromomethyl) naphthalene (1.16 g, 4.72 mmol) was added at room temperature and stirred for 1 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from benzene gave 1-cyano-4-(2,2-dicyano-5-methyl-4-hexenyl)naphthalene (**1b**, 0.760 g, 2.54 mmol, 59% yield). Colorless solid; mp 225–226 °C (benzene); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.75 (s, 3H), 1.87 (s, 3H), 2.85 (d, J = 7.3 Hz, 2H), 3.75 (s, 2H), 5.39–5.42 (m, 1H), 7.69–8.36 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.9, 26.4, 37.5, 38.5, 39.2, 109.3, 111.8, 114.2, 115.0, 117.3, 124.1, 126.4, 128.1, 128.2, 128.9, 131.7, 131.8, 132.8, 134.5, 141.6 ppm; IR (KBr) ν 2223 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 299 (8, M^+), 166 (57, $C_{12}H_8N$), 69 (100, C_5H_9); Anal. Calcd for $C_{20}H_{17}N_3$ C: 80.24, H: 5.72, N: 14.04. Found C: 80.39, H: 5.65, N: 13.95.

4.5. Photoreaction of **1a**

A dry CH_3CN (30 mL) solution of **1a** (226 mg, 0.900 mmol) was irradiated for 4 h. H_2O (3 mL) was added and left it as it is for 12 h. The mixture contained ***syn*-2a**, ***anti*-2a**, and **3a**. Separation by column chromatography on silica gel (eluent; hexane:AcOEt = 5:1) gave *syn*-4-(prop-1-en-2-yl)-4,5-dihydro-2*H*,2′*H*-spiro[furan-3,1′-naphthalene]-4′-carbonitrile (***syn*-2a**, 97.1 mg, 0.387 mmol, 43% yield) and *anti*-4-(prop-1-en-2-yl)-4,5-dihydro-2*H*,2′*H*-spiro[furan-3,1′-naphthalene]-4′-carbonitrile (***anti*-2a**). Data for ***syn*-2a**: colorless solid; mp 94–96 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (s, 3H), 2.55 (dd, J = 18.3, 6.4 Hz, 1H), 2.70 (dd, J = 18.3, 3.0 Hz, 1H), 2.83 (m, 1H), 3.81–4.11 (m, 3H), 4.25 (s, 1H), 4.39 (d, J = 8.7 Hz, 1H), 4.66 (s, 1H), 6.83 (dd, J = 6.4, 3.0 Hz, 1H), 7.32–7.50 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.5, 30.0, 34.9, 47.7, 56.8, 72.1, 78.4, 114.4, 115.1, 116.8, 125.0, 126.7, 127.7, 129.5, 135.4, 141.0, 141.3 ppm; IR (KBr) ν 2222 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 251 (5, M^+), 166 (100, $C_{12}H_8N$). Data for ***anti*-2a**: colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72 (s, 3H), 2.47–2.56 (m, 2H), 2.87 (t, J = 6.3 Hz, 1H), 3.86–4.10 (m, 4H), 4.87 (s, 1H), 5.00 (t, J = 1.6 Hz, 1H), 6.85 (t, J = 4.3 Hz, 1H), 7.30-7.54 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.9, 29.3, 48.1, 54.4, 71.6, 109.3, 114.5, 116.9, 125.3, 125.5, 127.6, 129.8, 138.9, 142.7, 143.8 ppm.

4.6. Photoreaction of **1b**

A dry CH_3CN (100 mL) solution of **1b** (100.0 mg, 0.333 mmol) was irradiated for 1 h. H_2O (11 mL) was added and left it as it is for 12 h. The mixture contained ***syn*-2b**, ***anti*-2b**, and **3b**. Separation by column chromatography on silica gel (eluent; hexane:AcOEt = 5:1) gave *syn*-2-(prop-1-en-2-yl)-2′*H*-spiro[cyclopentane-1,1′-naphthalene]-4,4,4′-tricarbonitrile (***syn*-2b**) and 4,4-dimethyl-3,3a,4,5-tetrahydro-5,9b-ethenocyclopenta[*a*]naphthalene-2,2,5(1*H*)-tricarbonitrile (**3b**, 23.7 mg, 0.079 mmol, 24% yield). Data for ***syn*-2b**: colorless solid; mp 154–156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (s, 3H), 2.55–2.87 (m, 6H), 3.17 (d, J = 15.0 Hz, 1H), 4.30 (s, 1H), 4.80 (s, 1H), 6.80 (dd, J = 5.9, 3.6 Hz, 1H), 7.17–7.54 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.4, 31.1, 38.7, 43.2, 48.5, 50.4, 56.8, 115.5, 115.7, 116.1, 116.3, 117.5, 125.9, 128.6, 129.5, 129.8, 135.1, 140.4, 140.8 ppm; GC–MS (EI) m/z (%) = 299 (2, M^+), 166 (100, $C_{12}H_8N$). Data for **3b**: colorless solid; mp 153–155 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (s, 3H), 1.39 (s, 3H), 2.11 (dd, J = 3.6, 1.8 Hz, 1H), 2.50 (dd, J = 11.8, 6.5 Hz, 1H), 2.79 (dd, J = 13.7, 6.3 Hz, 1H), 2.95 (d, J = 15.4 Hz, 1H), 3.34 (d, J = 15.2 Hz, 1H), 6.24 (d, J = 2.7 Hz, 1H), 6.41 (d, J = 2.7 Hz, 1H), 7.33–7.60 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.7, 30.1, 30.8, 37.2, 41.1, 46.2, 49.4, 51.3, 59.0, 115.4, 117.4, 119.5, 126.5, 127.7, 128.5, 129.4, 129.9, 137.8, 140.7, 142.8 ppm; GC–MS (EI) m/z (%) = 299 (5, M^+), 166 (54, $C_{12}H_8N$).

4.7. Preparation of **1a-d_6**

A mixture of ethyl bromoacetate (11.3 g, 67.4 mmol) and $P(OEt)_3$ (13.2 g, 79.7 mmol) was refluxed at 150 °C for 3 h. Concentration in vacuo gave ethyl 2-(diethylphosphoryl) acetate [75] (15.2 g, 67.4 mmol, 99% yield). Data for ethyl 2-(diethylphosphoryl) acetate: colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (m, 9H), 2.96 (d, J = 21.6 Hz, 2H), 4.18 (m, 6H) ppm. To a THF (150 mL) solution of ethyl 2-(diethylphosphoryl) acetate (15.2 g, 67.4 mmol) was slowly added *n*-BuLi (1.6 M hexane solution, 60 mL, 96 mmol) at −78 °C and stirred for 30 min. Acetone-d_6 (15 mL, 200 mmol) was added at −50 °C and stirred for 30 min, then stirred at room temperature for 2 h. Sat. NH_4Cl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Distillation under reduced pressure (bp 69–71 °C/40 mmHg) gave ethyl 3,3-bis(trideuteriomethyl)-2-propenoate (6.69 g, 49.9 mmol, 74% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, J = 7.1 Hz, 3H), 4.14 (q, J = 7.1 Hz, 2H), 5.67 (s, 1H) ppm. To THF (40 mL) solution of ethyl 3,3-bis(trideuteriomethyl)-2-propenoate (3.35 g, 25.0 mmol) was slowly added ^{i}Bu$_2$AlH (1.0 M hexane solution, 100 mL, 100 mmol) at −78 °C, and stirred for 30 min. Then the solution was stirred at room temperature for 1 h. After cooling to 0 °C, wet Na_2SO_4 was added and stirred for 1 h. The precipitated colorless solid was collected, washed with Et_2O, and concentrated in vacuo. Distillation under reduced pressure (bp 76–77 °C/50 mmHg) gave 3,3-bis(trideuteriomethyl)-2-propen-1-ol (0.817 g, 8.88 mmol, 36% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15 (br, 1H), 4.12 (br, 2H), 5.41 (t, J = 7.1, 1H) ppm. To a mixture of THF (10 mL) and NaH (0.540 g, 13.3 mmol) was added 3,3-bis(trideuteriomethyl)-2-propen-1-ol (0.817 g, 8.88 mmol) at

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room temperature, and then refluxed for 30 min. THF (70 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (1.97 g, 7.99 mmol) was added at 0 °C and stirred for 1 h. Then the solution was warmed to room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 1-cyano-4-{5,5-[bis(trideuteriomethyl)]-2-oxa-4-pentenyl}naphthalene (**1a-*d*$_6$**, 0.570 g, 1.87 mmol, 28% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13 (d, J = 6.9 Hz, 2H), 4.98 (s, 2H), 5.44 (m, 1H), 7.62–8.29 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.5, 26.2, 67.4, 69.7, 110.2, 117.9, 120.5, 124.4, 124.5, 125.8, 127.6, 128.2, 131.0, 132.2, 132.4, 138.0, 140.3 ppm; GC–MS (EI) m/z (%) = 257 (7, M^+), 166 (62, $C_{12}H_8N$), 91 (98, $C_5H_3D_6$).

4.8. Preparation of **1b-*d*$_6$**

A mixture of 3,3-bis(trideuteriomethyl)-2-propen-1-ol (1.07 g, 11.6 mmol) and HBr (47% aq, 30 mL) was vigorously shaken. Upper layer was separated to be identified as 1,1-bis(trideuteriomethyl)-3-bromo-1-propene. To a mixture of THF (10 mL) and NaH (0.510 g, 12.8 mmol) was added malononitrile (3.83 g, 58.0 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (5 mL) solution of the 1,1-bis(trideuteriomethyl)-3-bromo-1-propene was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 4,4-dicyano-1,1-bis(trideuteriomethyl)-1-butene (0.386 g, 2.76 mmol, 24% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73 (s, 3H), 1.80 (s, 3H), 2.73 (dd, J = 6.6, 1.3 Hz, 2H), 3.67 (t, J = 6.6 Hz, 1H), 5.22 (t, J = 1.3 Hz, 1H) ppm. To a mixture of THF (10 mL) and NaH (0.144 g, 3.59 mmol) was added 4,4-dicyano-1,1-bis(trideuteriomethyl)-1-butene (0.386 g, 2.76 mmol) under argon atmosphere at room temperature, and stirred for 1 h. THF (30 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (0.883 g, 3.59 mmol) was added and stirred for 4 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from benzene gave 1-cyano-4-{2,2-dicyano-5,5-[bis(trideuteriomethyl)]-4-pentenyl}naphthalene (**1b-*d*$_6$**, 0.102 g, 0.333 mmol, 12% yield). Colorless solid; mp 219–221 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.85 (s, 2H), 3.74 (s, 2H), 5.40 (m, 1H), 7.68–8.36 (m, 6H) ppm; GC–MS (EI) m/z (%) = 305 (8, M^+), 166 (100, $C_{12}H_8N$).

4.9. Preparation of **1c**

To a THF (100 mL) solution of ethyl 2-(diethylphosphoryl) acetate (8.80 g, 39.1 mmol) was slowly added n-BuLi (1.6 M hexane solution, 32.0 mL, 51.2 mmol) at −78 °C under argon atmosphere and stirred for 30 min. Cyclohexanone (8.0 mL, 77.2 mmol) was added at −50 °C and stirred for 30 min, then stirred at room temperature for 2 h. Sat. NH_4Cl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Distillation under reduced pressure (bp 78–81 °C/3 mmHg) gave ethyl cyclohexylideneacetate (5.91 g, 35.2 mmol, 90% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, J = 7.2 Hz, 3H), 1.60-1.65 (m, 6H), 2.18 (m, 2H), 2.81 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 5.59 (s, 1H) ppm. To THF (100 mL) solution of ethyl cyclohexylideneacetate (4.20 g, 25.0 mmol) was slowly added ^{i}Bu$_2$AlH (1.0 M hexane solution, 100 mL, 100 mmol) at −78 °C, stirred for 30 min. Then the solution was stirred at room temperature for 1 h. After cooling to 0 °C, wet Na_2SO_4 was added and stirred for 1 h. The precipitated colorless solid was collected, washed with Et_2O, and concentrated in vacuo. Distillation under reduced pressure (bp 88–90 °C/7 mmHg) gave (2-hydroxyethylidene) cyclohexane (1.33 g, 10.6 mmol, 42% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89–1.61 (m, 7H), 2.11–2.21 (m, 4H), 4.13 (dd, J = 7.0 Hz, 0.4 Hz, 2H), 5.36 (m, 1H) ppm. A mixture of (2-hydroxyethylidene) cyclohexane (0.750 g, 5.95 mmol) and HBr (47% aq, 20 mL) was vigorously shaken. Upper layer was separated to be identified as (2-bromoethylidene)cyclohexane. To a mixture of THF (5 mL) and NaH (0.286 g, 7.15 mmol) was added malononitrile (0.786 g, 11.9 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (5 mL) solution of the (2-bromoethylidene) cyclohexane was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 3,3-dicyanopropylidenecyclohexane (0.410 g, 2.36 mmol, 40% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43–1.58 (m, 6H), 2.16–2.19 (m, 4H), 2.74 (dd, J = 7.6, 6.8 Hz, 2H), 3.66 (t, J = 6.8 Hz, 2H), 5.15 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.82, 26.82, 28.14, 28.64, 29.08, 29.39, 37.45, 111.83 (2C), 112.57, 148.39 ppm; GC–MS (EI) m/z (%) = 174 (17, M^+), 109 (65, C_8H_{13}), 67 (100, C_5H_7). To a mixture of THF (2 mL) and NaH (0.123 g, 3.07 mmol) was added 3,3-dicyanopropylidenecyclohexane (0.410 g, 2.36 mmol) under argon atmosphere at room temperature, and stirred for 1 h. THF (20 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (0.581 g, 2.36 mmol) was added and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from EtOH gave 1-cyano-4-(2,2-dicyano-4-cyclohexylidenebutyl)naphthalene (**1c**, 0.304 g, 0.842 mmol, 36% yield). Colorless solid; mp 179–181 °C (EtOH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 6H), 2.22–2.24 (m, 4H), 2.87 (d, J = 7.5 Hz, 2H), 3.74 (s, 2H), 5.33 (m, 1H), 7.69–7.79 (m, 3H), 7.96 (d, J = 7.6, 1H), 8.18 (m, 1H), 8.35 (m,1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.81, 28.12, 28.71, 29.71, 36.50, 37.71, 38.42, 39.38, 109.31, 110.81 (2C), 111.67, 115.04, 117.37, 124.08, 126.34, 128.86, 131.65, 131.79, 132.77, 134.52, 149.51 ppm; IR(KBr) ν 2222 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 339 (3, M^+), 166 (13, $C_{12}H_8N$), 109 (100, C_8H_{13}); Anal. Calcd for $C_{23}H_{21}N_3$ C: 81.38, H: 6.24, N: 12.38. Found C: 80.88, H: 6.27, N: 12.24.

4.10. Photoreaction of **1c**

A dry CH_3CN (80 mL) solution of **1c** (271 mg, 0.800 mmol) was irradiated for 3 h. H_2O (9 mL) was added and left it as it is for 12 h. The mixture contained ***syn*-2c** and ***anti*-2c**. Yields and *syn*/*anti* ratio were determined by ^{1}H NMR to be 91% and 83:17, respectively. Separation by column chromatography on silica gel (eluent; hexane–AcOEt), recycling preparative HPLC (eluent; $CHCl_3$), and recrystallization from hexane–MeOH gave ***syn*-2c** (68.8 mg, 0.203 mmol, 25% yield). Colorless solid; mp 134–136 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21–1.82 (m, 8H), 2.48–2.92 (m, 6H), 3.21 (d, J = 15.3 Hz, 1H), 4.80 (m, 1H), 6.78 (dd, J = 6.4, 3.0 Hz, 1H), 7.13–7.54 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.0, 23.1, 25.7, 29.5, 30.9, 38.8, 42.6, 48.3, 50.3, 58.0, 115.0, 116.3, 116.5, 117.7, 125.5, 125.9, 127.5, 128.5, 129.6, 129.8, 132.3, 135.3, 140.5 ppm; IR (KBr) ν 2223 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 339 (6, M^+), 166 (100, $C_{12}H_8N$).

4.11. Preparation of **Z-7a**

To THF (80 mL) solution of ethyl acetoacetate (3.95 g, 30.4 mmol) was slowly added $(Me_3Si)_2NLi$ (1.0 M THF solution,

Please cite this article in press as: H. Maeda, et al., Preparation of polycyclic compounds by intramolecular photospirocyclization and photocycloaddition reactions of 4-alkenyl-1-cyanonaphthalene derivatives, J. Photochem. Photobiol. A: Chem. (2016), http://dx.doi.org/10.1016/j.jphotochem.2016.01.005

36.5 mL, 36.5 mmol) at –60 °C under argon atmosphere, and stirred for 2 h. *p*-Toluenesulfonic anhydride was added and stirred for 12 h. Sat. NaCl aq and AcOEt were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave ethyl 3-(toluene-4-sulfonyloxy)-but-2-enoate [76] (8.40 g, 29.6 mmol, 97% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, J = 7.2 Hz, 3H), 2.10 (m, 3H), 2.44 (s, 3H), 4.04 (q, J = 7.2 Hz, 2H), 5.48 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H) ppm. To THF (80 mL) solution of 3-(toluene-4-sulfonyloxy)-but-2-enoate (8.40 g, 29.6 mmol), $PhB(OH)_2$ (5.41 g, 44.4 mmol), and $PdCl_2(PPh_3)_2$ (1.04 g, 1.48 mmol) was added Na_2CO_3 aq (2 M, 45 mL, 90 mmol), and stirred at 60 °C for 15 h. AcOEt was added, and the organic layer was washed with NaOH aq and then sat. NaCl aq. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Distillation under reduced pressure (bp 121–124 °C/7 mmHg) gave ethyl (*Z*)-3-phenyl-but-2-enoate (4.71 g, 24.8 mmol, 84% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (t, J = 7.1 Hz, 3H), 2.18 (s, 3H), 4.00 (q, J = 7.1 Hz, 2H), 5.90 (m, 1H), 7.16–7.35 (m, 5H) ppm. To THF (60 mL) solution of ethyl (*Z*)-3-phenyl-but-2-enoate (4.71 g, 24.8 mmol) was slowly added ^{i}Bu_2AlH (1.0 M hexane solution, 65 mL, 65 mmol) at −78 °C under argon atmosphere, and stirred for 30 min. Then the solution was stirred at room temperature for 1 h. After cooling to 0 °C, wet Na_2SO_4 was added and stirred for 1 h. The precipitated colorless solid was collected, washed with Et_2O, and concentrated in vacuo. The product, (*Z*)-3-phenylbut-2-en-1-ol (2.68 g, 18.1 mmol, 73% yield) was used without purification. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25 (br, 1H), 2.10 (s, 3H), 4.08 (m, 2H), 5.72 (m, 1H), 7.16–7.37 (m, 5H) ppm. A Et_2O (20 mL) solution of (*Z*)-3-phenylbut-2-en-1-ol (2.68 g, 18.1 mmol), PPh_3 (4.72 g, 18.0 mmol), CBr_4 (5.97 g, 18.0 mmol) was stirred at room temperature for 2 h. The precipitated solid was removed by filtration. The solution was concentrated in vacuo. The product, (*Z*)-2-phenyl-4-bromo-2-butene was used without purification. To a mixture of THF (5 mL) and NaH (0.869 g, 21.7 mmol) was added malononitrile (2.39 g, 36.2 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (5 mL) solution of (*Z*)-2-phenyl-4-bromo-2-butene was added, and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave (*Z*)-5,5-dicyano-2-phenyl-2-pentene [77] (1.52 g, 7.76 mmol, 43% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.12 (m, 3H), 2.67 (m, 2H), 3.60 (t, J = 6.8 Hz, 1H), 5.53 (m, 1H), 7.30–7.45 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.0, 23.3, 30.5, 112.4, 117.9, 125.9, 127.9, 128.4, 142.1, 142.8 ppm; GC–MS (EI) m/z (%) = 196 (10, M^+), 131 (100, $C_{10}H_{11}$). To THF (5 mL) solution of NaH (0.398 g, 9.95 mmol) was added (*Z*)-5,5-dicyano-2-phenyl-2-pentene (1.50 g, 7.65 mmol) at room temperature under argon atmosphere, and stirred for 1 h. THF (30 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (1.88 g, 7.65 mmol) was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from EtOH gave (*Z*)-1-cyano-4-(2,2-dicyano-5-phenyl-4-hexenyl)naphthalene (***Z*-7a**, 1.16 g, 3.21 mmol, 42% yield). Pale yellow solid; mp 161–163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.17 (m, 3H), 2.80 (d, J = 7.3 Hz, 2H), 3.60 (s, 2H), 5.69 (m, 1H), 7.12–8.33 (m, 11H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.5, 38.0, 38.4, 38.8, 111.7, 114.9, 116.6, 117.3, 124.0, 126.3, 127.5, 127.6, 127.9, 128.1, 128.6, 128.8, 131.6, 132.7, 134.3, 140.1, 146.0 ppm; IR (KBr) ν 2222 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 361 (8, M^+), 166 (22, $C_{12}H_8N$), 131 (100, $C_{10}H_{11}$); Anal. Calcd for $C_{25}H_{19}N_3$ C: 83.08, H: 5.30, N: 11.63. Found C: 83.08, H: 5.42, N: 11.50.

4.12. Preparation of *E*-7a

To a THF (100 mL) solution of ethyl 2-(diethylphosphoryl) acetate (15.8 g, 70.0 mmol) was added *n*-BuLi (1.6 M hexane solution, 52.5 mL, 84 mmol) slowly at −78 °C under argon atmosphere and stirred for 30 min. Acetophenone (12.3 mL, 105 mmol) was added at −50 °C and stirred for 30 min, then stirred at room temperature for 2 h. Sat. NH_4Cl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Distillation under reduced pressure (bp 131–132 °C/8 mmHg) gave ethyl (*E*)-3-phenylbut-2-enoate (8.69 g, 45.7 mmol, 65% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (t, J = 7.0 Hz, 3H), 2.58 (d, J = 1.2 Hz, 3H), 4.22 (q, J = 7.0 Hz, 2H), 6.13 (q, J = 1.3 Hz, 1H), 7.32–7.49 (m, 5H) ppm. To THF (110 mL) solution of ethyl (*E*)-3-phenylbut-2-enoate (8.69 g, 45.7 mmol) was slowly added ^{i}Bu_2AlH (1.0 M hexane solution, 110 mL, 110 mmol) at −78 °C under argon atmosphere, and stirred for 30 min. Then the solution was stirred at room temperature for 1 h. After cooling to 0 °C, wet Na_2SO_4 was added and stirred for 1 h. The precipitated colorless solid was collected, washed with Et_2O, and concentrated in vacuo. The product, (*E*)-3-phenylbut-2-en-1-ol (6.70 g, 45.2 mmol, 99% yield) was used without purification. Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (br, 1H), 2.08 (s, 3H), 4.36 (m, 2H), 6.00 (m, 1H), 7.26–7.41 (m, 5H) ppm. A mixture of (*E*)-3-phenylbut-2-en-1-ol (6.70 g, 45.2 mmol) and HBr (47% aq, 30 mL) was vigorously shaken. Upper layer was separated to be identified as (*E*)-4-bromo-2-phenyl-2-butene. To a mixture of THF (30 mL) and NaH (2.19 g, 54.8 mmol) was added malononitrile (6.03 g, 91.4 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (5 mL) solution of the (*E*)-4-bromo-2-phenyl-2-butene was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave (*E*)-5,5-dicyano-2-phenyl-2-pentene (5.62 g, 28.7 mmol, 63% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.16 (m, 3H), 2.97 (m, 2H), 3.80 (t, J = 6.8 Hz, 1H), 5.75 (m, 1H), 7.30-7.40 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.0, 23.3, 30.5, 112.4, 117.9, 125.9, 127.9, 128.4, 142.1, 142.8 ppm; GC–MS (EI) m/z (%) = 196 (10, M^+), 131 (100, $C_{10}H_{11}$). To THF (10 mL) solution of NaH (0.331 g, 8.27 mmol) was added (*E*)-5,5-dicyano-2-phenyl-2-pentene (1.35 g, 6.89 mmol) at room temperature under argon atmosphere, and stirred for 1 h. THF (30 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (1.69 g, 6.89 mmol) was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from benzene gave (*E*)-1-cyano-4-(2,2-dicyano-5-phenyl-4-hexenyl)naphthalene (***E*-7a**, 0.859 g, 2.38 mmol, 35% yield). Pale yellow solid; mp 178–180 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.16 (m, 3H), 3.07 (d, J = 7.1 Hz, 2H), 3.83 (s, 2H), 5.93 (m, 1H), 7.32–8.37 (m, 11H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4, 37.9, 38.6, 39.1, 111.9, 114.9, 116.9, 117.3, 124.0, 126.0, 126.4, 128.0, 128.2, 128.3, 128.5, 128.9, 131.7, 131.8, 132.8, 134.3, 142.1, 143.8 ppm; IR(KBr) ν 2222 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 361 (3, M^+), 166 (16, $C_{12}H_8N$), 131 (100, $C_{10}H_{11}$).

4.13. Photoreaction of *Z*-7a and *E*-7a

CH_3CN (28 mL) solution of ***Z*-7a** (100 mg, 0.277 mmol) was irradiated for 48 h. CH_3CN (28 mL) solution of ***E*-7a** (100 mg, 0.277 mmol) was also irradiated under the same conditions. From ^{1}H NMR spectra, yields (10% from ***Z*-7a**, 9% from ***E*-7a**) were determined. Mixture obtained by photoreaction from ***E*-7a** was separated by column chromatography on silica gel (eluent;

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hexane–AcOEt), recycling preparative HPLC (eluent; $CHCl_3$), recrystallization from EtOH to give (2a*R**,5a*S**,6*R**,10b*S**)-6-methyl-6-phenyl-5a,6-dihydrocyclobuta[*a*]cyclopenta[*b*]naphthalene-4,4,10b(3*H*,5*H*,10b*H*)-tricarbonitrile (**8**, 2.0 mg, 0.006 mmol, 2% yield). Colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.86 (s, 3H), 2.51–2.55 (m, 2H), 2.79 (d, J = 14.1 Hz, 1H), 3.01 (d, J = 14.1 Hz, 1H), 3.15 (m, 1H), 5.57 (d, J = 2.8 Hz, 1H), 6.01 (d, J = 2.8 Hz, 1H), 6.71–6.74 (m, 2H), 7.17–7.19 (m, 3H), 7.39–7.71 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.2, 31.0, 39.9, 45.7, 46.6, 48.4, 52.3, 57.4, 116.7, 116.7, 118.9, 126.9, 127.6, 128.3, 128.3, 129.1, 129.2, 129.9, 132.2, 137.3, 141.2, 141.9, 142.0 ppm; GC–MS (EI) m/z (%) = 361 (14, M^+), 166 (11, $C_{12}H_8N$), 131 (100, $C_{10}H_{11}$).

4.14. Photoreaction of *Z*-7a and *E*-7a in the presence of benzophenone

CH_3CN (8.0 mL) solution of ***Z*-7a** (10.0 mg, 0.028 mmol) and benzophenone (50.4 mg, 0.277 mmol) was irradiated for 6 h. CH_3CN solution of ***E*-7a** was also irradiated under the same conditions. Both solutions reached to the photostationary state (*E*:*Z* = 76:24). The ratio was determined by ^{1}H NMR.

4.15. Preparation of 7b

THF (70 mL) solution of ethyltriphenylphosphonium iodide (13.5 g, 32.5 mmol) and ^{t}BuOK (3.37 g, 30.0 mmol) was stirred under argon atmosphere for 5 min. The color of solution turned orange due to the formation of ylide. THF (40 mL) solution of benzophenone (4.56 g, 25.0 mmol) was added, and stirred at room temperature for 2 h, and refluxed overnight. Sat. NaCl aq and benzene were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the colorless oil by column chromatography on silica gel (eluent; hexane) gave 1,1-diphenylpropene (4.44 g, 22.9 mmol, 92% yield). Colorless solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.77 (d, J = 7.0 Hz, 3H), 6.18 (q, J = 7.0 Hz, 1H) 7.17–7.40 (m, 10H) ppm. CCl_4 (30 mL) solution of 1,1-diphenylpropene (2.08 g, 10.7 mmol), *N*-bromosuccinimide (1.91 g, 10.7 mmol), benzoyl peroxide (cat) was refluxed for 2 h. The precipitated solid was removed by filtration. The solution was concentrated in vacuo. The product, 3-bromo-1,1-diphenylpropene (2.91 g, 10.6 mmol, 99% yield) was used without purification. Yellow solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.06 (d, J = 8.5 Hz, 2H), 6.34 (t, J = 8.5 Hz, 1H), 7.22–7.42 (m, 10H) ppm. To a mixture of THF (10 mL) and NaH (0.700 g, 17.5 mmol) was added malononitrile (1.05 g, 15.9 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. THF (20 mL) solution of 3-bromo-1,1-diphenylpropene was added, and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 4,4-dicyano-1,1-diphenyl-1-butene (1.39 g, 5.40 mmol, 51% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.86 (dd, J = 7.3 Hz, 6.8 Hz, 2H), 3.73 (t, J = 6.8 Hz, 1H), 6.09 (t, J = 7.4 Hz, 1H), 7.18–7.43 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.3, 31.2, 112.2 (2C), 118.5, 127.4, 128.0, 128.2, 128.3, 128.7, 129.4, 148.7 ppm; GC–MS (EI) m/z = 258 (6, M^+), 193 (46, $C_{15}H_{13}$), 115 (100, C_9H_7). To THF (5 mL) solution of NaH (0.168 g, 4.19 mmol) was added 4,4-dicyano-1,1-diphenyl-1-butene (0.721 g, 2.79 mmol) at room temperature under argon atmosphere, and stirred for 1 h. THF (20 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (0.687 g, 2.79 mmol) was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from EtOH gave 1-cyano-4-(2,2-dicyano-5,5-diphenyl-4-pentenyl)naphthalene (**7b**, 0.418 g, 0.980 mmol, 35% yield). Pale green solid; mp 178–179 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.95 (d, J = 7.4 Hz, 2H), 3.68 (s, 2H), 6.25 (t, J = 7.4 Hz, 1H), 7.15–7.41 (m, 10H), 7.59 (d, J = 7.4 Hz, 1H), 7.69–7.76 (m, 2H), 7.90 (d, J = 7.4 Hz, 1H), 8.06-8.34 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.5, 38.8, 111.7 (2C), 114.8, 117.3, 117.7, 124.0, 126.4, 127.5, 128.0, 128.2, 128.4, 128.7, 128.9, 129.5, 131.7, 132.7, 134.1, 138.2, 140.6, 149.4 ppm; IR(KBr) ν 2222 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 423 (3, M^+), 193 (100, $C_{15}H_{13}$); Anal. Calcd for $C_{30}H_{21}N_3$ C: 85.08, H: 5.00, N: 9.92. Found C: 84.83, H: 5.30, N: 9.80.

4.16. Photoreaction of 7b

CH_3CN (0.7 mL) solution of **7b** (8.9 mg, 0.021 mmol) was irradiated for 24 h. NMR spectrum indicated that no reaction took place.

4.17. Preparation of 11a

CCl_4 (50 mL) solution of cyclopentene (3.40 g, 50.0 mmol), *N*-bromosuccinimide (8.90 g, 50.0 mmol), benzoyl peroxide (cat) was refluxed for 1 h. The precipitated solid was removed by filtration. The solution was concentrated in vacuo. The product, 3-bromocyclopentene was used without purification. To a mixture of THF (10 mL) and NaH (2.00 g, 50.0 mmol) was added malononitrile (3.30 g, 50.0 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. 3-Bromocyclopentene was added at room temperature, and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 3-(dicyanomethyl)cyclopentene (3.64 g, 27.6 mmol, 55% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.79 (m, 1H), 2.28–2.65 (m, 3H), 3.34 (m, 1H), 3.66 (d, J = 6.2 Hz, 1H), 5.73 (m, 1H), 6.14 (m, 1H) ppm. To THF (10 mL) solution of NaH (2.30 g, 33.1 mmol) was added 3-(dicyanomethyl)cyclopentene (3.64 g, 27.6 mmol) at room temperature under argon atmosphere, and stirred for 1 h. THF (50 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (6.79 g, 27.6 mmol) was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from EtOH gave 1-cyano-4-[2,2-dicyano-2-(2-cyclopentenyl)ethyl]naphthalene (**11a**, 1.68 g, 5.66 mmol, 21% yield). Colorless solid; mp 168–169 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.12 (m, 1H), 2.39–2.72 (m, 3H), 3.52 (m, 1H), 3.73 (s, 2H), 5.90 (m, 1H), 6.27 (m, 1H), 7.69–7.78 (m, 3H), 7.95 (d, J = 7.4 Hz, 1H), 8.17 (m, 1H), 8.33 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.8, 32.7, 37.1, 43.8, 54.5, 111.6, 114.6, 114.7, 117.4, 124.0, 126.0, 126.3, 128.0, 128.1, 128.8, 131.6, 131.8, 132.8, 134.6, 138.8 ppm; IR(KBr) ν 2221 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 297 (11, M^+), 166 (70, $C_{12}H_8N$), 67 (100, C_5H_7).

4.18. Preparation of 11b

CCl_4 (20 mL) solution of cyclohexene (5.18 g, 63.1 mmol), *N*-bromosuccinimide (11.4 g, 64.1 mmol), benzoyl peroxide (cat) was refluxed for 1 h. The precipitated solid was removed by filtration. The solution was concentrated in vacuo. The product, 3-bromocyclohexene was used without purification. To a mixture of THF (20 mL) and NaH (2.68 g, 67.0 mmol) was added malononitrile (4.02 g, 60.9 mmol) at 0 °C under argon atmosphere, and stirred for 1 h. 3-Bromocyclohexene was added at room temperature, and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; hexane–AcOEt) gave 3-(dicyanomethyl)

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cyclohexene (1.33 g, 9.10 mmol, 15% yield). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58–1.63 (m, 2H), 1.86 (m, 1H), 2.07-2.13 (m, 3H), 2.84 (m, 1H), 3.64 (d, J = 3.3 Hz, 1H), 5.65 (m, 1H), 6.07 (m, 1H) ppm. To THF (5 mL) solution of NaH (0.390 g, 9.76 mmol) was added 3-(dicyanomethyl)cyclohexene (1.19 g, 8.13 mmol) at room temperature under argon atmosphere, and stirred for 1 h. THF (50 mL) solution of 1-cyano-4-(bromomethyl)naphthalene (2.00 g, 8.13 mmol) was added at room temperature and stirred for 2 h. Sat. NaCl aq and Et_2O were added and shaken. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Separation of the brown oil by column chromatography on silica gel (eluent; $CHCl_3$) followed by recrystallization from EtOH gave 1-cyano-4-[2,2-dicyano-2-(2-cyclohexenyl)ethyl]naphthalene (**11b**, 1.59 g, 5.11 mmol, 62% yield). Colorless solid; mp 164–166 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (m, 2H), 2.02-2.33 (m, 4H), 3.00 (m, 1H), 3.74 (s, 2H), 5.89 (m, 1H), 6.23 (m, 1H), 7.70–7.79 (m, 3H), 7.96 (d, J = 7.4 Hz, 1H), 8.16 (m, 1H), 8.34 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 25.0, 25.9, 35.9, 43.8, 44.0, 111.6, 114.3, 114.6, 117.4, 122.1, 124.1, 126.3, 128.0, 128.1, 128.8, 131.6, 131.8, 132.8, 134.8, 135.0 ppm; IR(KBr) ν 2220 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 311 (3, M^+), 166 (89, $C_{12}H_8N$), 81 (100, C_6H_9); Anal. Calcd for $C_{21}H_{17}N_3$ C: 81.00, H: 5.50, N: 13.49. Found C: 80.88, H: 5.65, N: 13.25.

4.19. Photoreaction of **11a**

A dry CH_3CN (80 mL) solution of **11a** (238 mg, 0.800 mmol) was irradiated for 20 h. Separation by column chromatography on silica gel (eluent; hexane–AcOEt), recycling preparative HPLC (eluent; $CHCl_3$), and recrystallization from EtOH gave (2a*R**,2a^1*R**,2b^1*S**,6b*R**,8a*S**)-1,2,2a,2c,7,8a-hexahydrobenzo[*a*]cyclopropa[*cd*]pentaleno[1,6-*fg*]pentalene-2c,8,8(2a^1*H*,2b*H*,2b^1*H*)-tricarbonitrile (**12a**, 60.5 mg, 0.204 mmol, 25% yield). Colorless solid; mp 201–202 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.95 (m, 1H), 2.12–2.30 (m, 3H), 2.49 (d, J = 6.4 Hz, 1H), 2.74–2.82 (m, 2H), 3.12–3.19 (m, 3H), 3.60 (d, J = 6.4 Hz, 1H), 6.99 (m, 1H), 7.23–7.33 (m, 2H), 7.49 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.3, 30.8, 36.7, 38.6, 43.9, 47.0, 49.7, 51.3, 53.9, 66.7, 72.7, 115.0, 116.8, 119.1, 119.6, 125.0, 128.3, 128.5, 134.2, 146.7 ppm; IR (KBr) ν 2234 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 297 (71, M^+), 166 (100, $C_{12}H_8N$), 153 (83, $C_{11}H_7N$).

4.20. Photoreaction of **11b**

A dry CH_3CN (80 mL) solution of **11a** (249 mg, 0.800 mmol) was irradiated for 8 h. Separation by column chromatography on silica gel (eluent; hexane–AcOEt), recycling preparative HPLC (eluent; $CHCl_3$), and recrystallization from EtOH gave **12b** (73.0 mg, 0.235 mmol, 29% yield). Colorless solid; mp 232–233 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.48–2.01 (m, 6H), 2.49–2.70 (m, 4H), 2.97 (d, J = 4.7 Hz, 1H), 3.09 (d, J = 4.7 Hz, 1H), 3.51 (d, J = 6.7 Hz, 1H), 7.11 (m, 1H), 7.27–7.33 (m, 2H), 7.48 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.8, 21.6, 23.5, 29.4, 35.5, 41.3, 43.9, 46.3, 49.2, 54.1, 64.2, 66.5, 114.3, 116.7, 119.0, 120.3, 124.6, 128.2, 128.6, 134.2, 147.6 ppm; IR (KBr) ν 2233 (C≡N) cm^{-1}; GC–MS (EI) m/z (%) = 311 (47, M^+), 166 (38, $C_{12}H_8N$), 153 (100, $C_{11}H_7N$).

Acknowledgements

This study was partially supported financially by Grants-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformations of Carbon Resources” (18037063, 19020060 in the Area No. 444 to K.M.) and Scientific Research (C) (23550058 to K. M., 20550049, 23550047, 26410040 to H.M.) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan. H.M. is grateful for financial support from Mitsubishi Chemical Corporation Fund and The Mazda Foundation. This work was also supported by Kanazawa University SAKIGAKE Project. The authors also thank Dr. Akihiro Nomoto for X-ray crystallographic analysis of compound **8**.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2016.01.005.

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