Journal of Photochemistry and Photobiology A: Chemistry 337 (2017) 198–206

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Synthesis of pentacyclic compounds via intramolecular [3 + 2] photocycloaddition of cycloalkene linked naphthalenes

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ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form 4 January 2017
Accepted 7 January 2017
Available online 17 January 2017

Keywords:
Photocycloaddition
Naphthalene
Cycloalkene
Exciplex
Pentacyclic compounds

ABSTRACT

Intramolecular photocycloaddition reactions of cycloalkene linked naphthalenes lead to formation of pentacyclic compounds in a high yielding and stereoselective manner. Intramolecular [2 + 2] cycloadducts are formed initially in photoreactions of cycloalkene linked 1-cyanonaphthalenes. The initially formed intramolecular [2 + 2] cycloadducts absorb light at wavelengths used to promote the photochemical reactions and, as a result, they undergo efficient photocycloreversion to regenerate the starting substrates. In a less efficient competing process, the cycloalkene linked 1-cyanonaphthalenes react to form [3 + 2] intramolecular photoadducts, which do not absorb incident light under the conditions used. Consequently, these photoadducts become the major products in these processes. The relative configuration of the major diastereomers of the pentacyclic products formed from photoreactions of cyclopentene linked naphthalenes (*cis-cis*) differ from those (*cis-trans*) arising from the cyclooctene linked substrates. The results of theoretical calculations, which show that steric factors govern the preferred facial mode of intramolecular addition, are in good agreement with the stereochemical course of these photoreactions.

1. Introduction

Photocycloaddition reactions between unsaturated compounds such as arenes, alkenes, alkadienes, and alkynes have been extensively studied from both synthetic and mechanistic viewpoints [1–10]. Moreover, photocycloaddition reactions of arenes with cycloalkenes [11–30] or cycloalkadienes [31–42] has been utilized to synthesize various types of polycyclic compounds. Most of the previous studies have focused on reactions in which benzene and its derivatives serve as the arene substrates [11–25,31,32]. Consequently, studies of photocycloaddition reactions between cycloalkenes or cycloalkadienes and naphthalene derivatives are limited [11,26–28,33–37]. Thus far, the only processes of this type that have been described are those involving photocycloadditions of naphthalene or cyanonaphthalenes with cyclopentene [26,27], cyclooctene [11,28], cyclohexadiene [33–36], and norbornadiene [37]. Unfortunately, the chemical yields and product selectivities of these processes are not high. For example, intermolecular photocycloaddition of 1-cyanonaphthalene with 1,2-dimethylcyclopentene gives rise to two 1,2-[2 + 2] photocycloadducts while the major product is 1-azetine derivative [26] (Scheme 1(a)). In addition, photocycloaddition of naphthalene with *trans*-cyclooctene produces both 1,3-[3 + 2] and 1,4-[4 + 2] photocycloadducts in low chemical yields, whereas *cis*-cyclooctene does not participate in a photoreaction carried out under the same irradiation conditions [28] (Scheme 1(b)). In contrast to intermolecular reactions, the intramolecular counterparts often take place with high levels of regio- and stereo-selectivity owing to the close and pre-established locations of the reactive centers [43–51]. As we have described previously, photoreaction of alkene linked 1-cyanonaphthalenes generate tetracyclic products as single stereoisomers in high yields [52–54] (Scheme 1(c)). In the current effort, we carried out a study of intramolecular photoreactions of naphthalenes containing linked cycloalkenes with the aim of developing efficient and selective methods for the synthesis of pentacyclic compounds. The results of this investigation are described below.

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http://dx.doi.org/10.1016/j.jphotochem.2017.01.008
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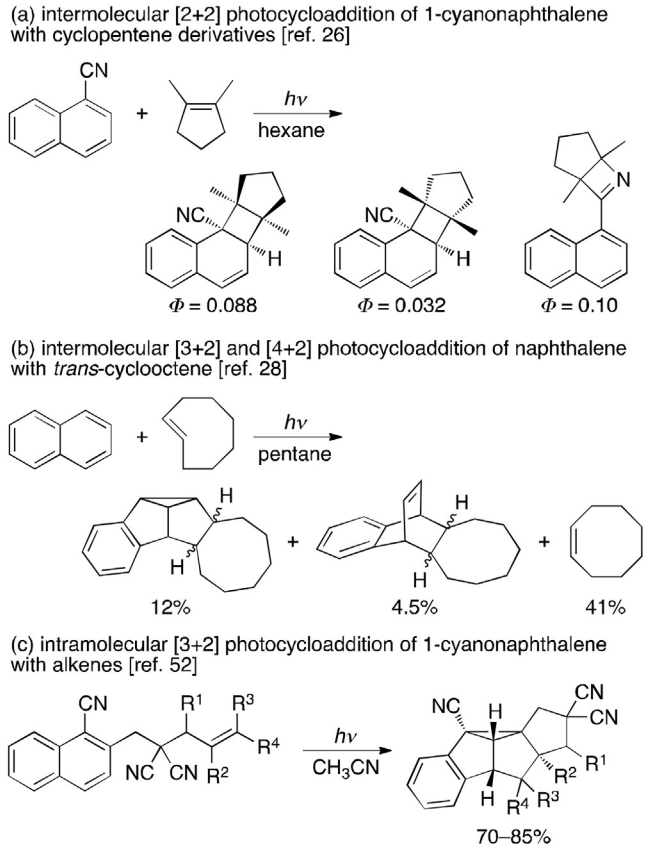
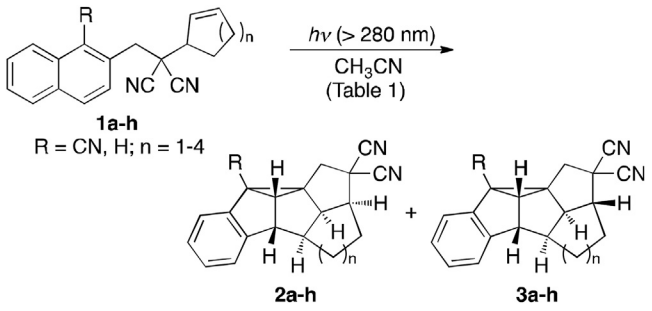


Scheme 1. Photocycloadditions of naphthalenes with alkenes.

2. Results and discussion

In the initial phase of this study, we explored the photochemistry of the cyclopentene linked 1-cyanonaphthalenes **1** (Scheme 2). Irradiation (>280 nm light) of a CH_3CN solution containing the 1-cyanonaphthalene derivative **1a** (R = CN, n = 1) in a Pyrex glass vessel under an argon atmosphere by using a high-pressure mercury lamp gave rise to formation of the pentacyclic product **2a** as a single stereoisomer in 74% isolated yield (Scheme 2, Table 1, entry 1) [52]. In a similar manner, photoreaction of the cyclohexene-linked cyanonaphthalene **1b** (R = CN, n = 2) also produced the corresponding pentacyclic product **2b** in 85% yield (entry 2). However, photoreaction of the cycloheptene linked substrate **1c** (R = CN, n = 3) generated the corresponding product **2c** in only a 20% yield along with the stereoisomer **3c** (51%) (entry 3). Finally, photoreaction of the analogous cyclooctene linked substrate **1d** (R = CN, n = 4) exclusively produced stereoisomer **3d** (61%, entry 4). When related substances **1e–g** (R = H, n = 1-3)



Scheme 2. Synthesis of pentacyclic compounds by using intramolecular photocycloaddition.

Table 1
Effects of substituents and ring size of cycloalkenes on intramolecular photocycloadditions of naphthalene derivatives.[a]

Entry	Substrate	R	n	[1] (mM)	Time (h)	Yields[b] (%)	
						2	**3**
1	**1a**	CN	1	30	25	74	0
2	**1b**	CN	2	30	10	85	0
3	**1c**	CN	3	10	7	20	51
4	**1d**	CN	4	5	20	0	61
5	**1e**	H	1	10	300	0	0
6	**1f**	H	2	10	300	<1	<1
7	**1g**	H	3	20	300	<1	<1
8	**1h**	H	4	5	70	0	76

[a] Photoreactions of **1a–h** (>280 nm light using Pyrex glass vessel, high-pressure mercury lamp) were carried out in CH_3CN under an argon atmosphere.
[b] Isolated yields.

lacking the cyano group on the naphthalene ring are subjected to photoreactions under the same conditions, photoproducts are not formed (< 1% yield) and starting materials are nearly completely recovered even following prolonged periods of irradiation (entries 5–7). However, photoreaction of cyclooctene linked naphthalene derivative **1h** (R = H, n = 4) does take place to generate **3h** in 76% yield (entry 8).

The structures of the photoproducts produced in the above reactions were determined by using spectral methods. Especially informative information came from X-ray crystallographic analysis of **2a** [52], **2b**, **2c**, **3d** and **3h** (Fig. 1). The crystal structures demonstrate that all ring fusions rising by formation of bonds to the alkene carbons are *cis* and that the junctions originating by formation of bonds to the allylic carbon differ depending on the substrate in the following manner, *cis* in **2a–c** and *trans* in **3d,h**.

The unique behavior of cyclooctene linked cyanonaphthalene **1d** prompted us to explore this photoreaction in more detail. We observed that in the photoreaction an initial product was formed efficiently and then it disappeared upon continued irradiation. In a previous study, we showed that intramolecular photocycloaddition reactions proceed more slowly in benzene than in CH_3CN [52]. Thus, to facilitate optimized formation of the initial photoproduct, reaction of **1d** was carried out in benzene. Photoreaction in this solvent led to production of the initial product in 8% yield after 3 h irradiation. The ^1H NMR spectrum of this substance contains resonances for two coupled vinyl hydrogens at 5.83 (d, J = 9.9 Hz, 1H) and 6.47 (d, J = 9.9 Hz, 1H) ppm and two resonances ascribable to hydrogens on a cyclobutane ring at 2.53 and 2.58 ppm. Based on these observations, the initially formed photoproduct was identified as the intramolecular [2 + 2] photocycloadduct **4d** (Scheme 3, R = CN, n = 4). Indeed, irradiation of a CH_3CN solution of **4d** led to exclusive formation of **1d**.

The time dependence of the photoreaction of **1d** in CD_3CN was monitored by using ^1H NMR spectroscopy (Fig. 2(a)). The results show that **1d** disappears within 20 min of the start of irradiation and [2 + 2] photocycloadduct **4d** is formed. The amount of **1d** decreases upon further irradiation and finally **3d** is produced as the only product. The time course of photoreaction of **1h**, the cyclooctene linked naphthalene that does not contain a cyano group, was also monitored (Fig. 2(b)). The consumption of **1h** was found to be slower than that of **1d** and no substance other than **3h** could be detected in the crude product mixture.

These results enabled us to propose the mechanistic pathway shown in Scheme 3 for the intramolecular photocycloaddition reactions. Upon irradiation, the cycloalkene linked 1-cyanonaphthalenes **1a-d** undergo initial intramolecular 1,2-[2 + 2] photocycloadditon to form **4** via the intermediacy of intramolecular singlet exciplexes. Owing to the fact that **4** possesses a styrene chromophore, it absorbs light in the >280 nm region used to

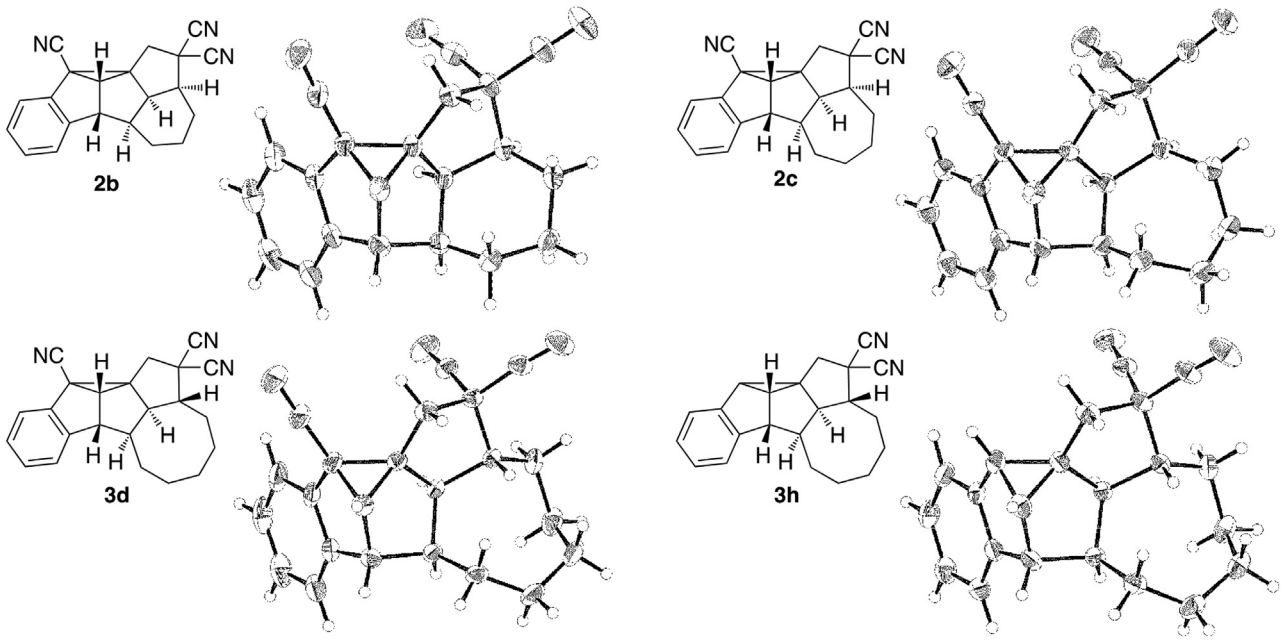
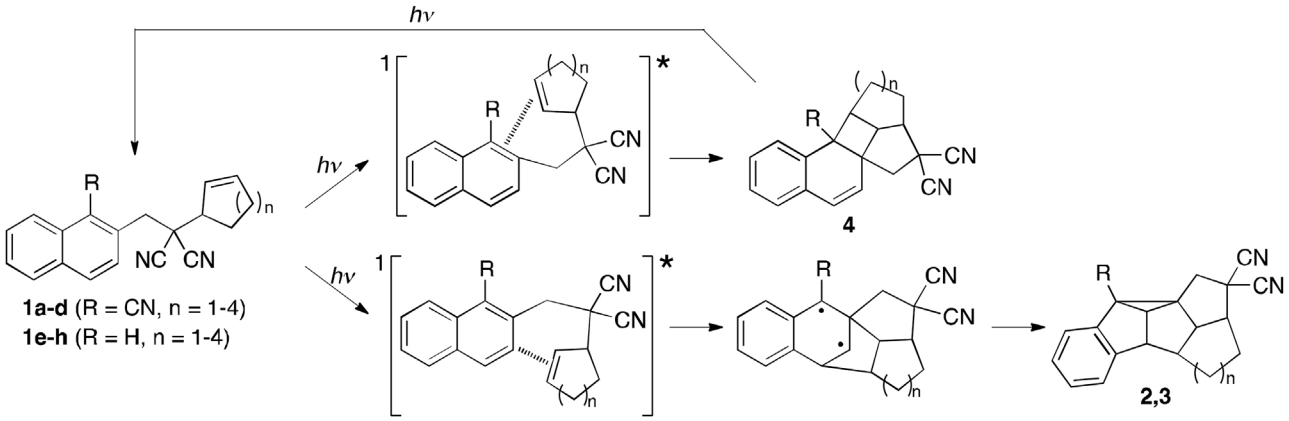


Fig. 1. ORTEP plots of X-ray crystallographic data of products.



Scheme 3. Possible mechanistic pathways for intramolecular photocycloaddition reactions.

promote these processes. Consequently, it undergoes cycloreversion to form the starting material **1** as part of a photochemically promoted equilibrium process. Formation of pentacyclic products **2** and **3** then takes place by a less efficient sequential 2,4-[3 + 2] photocycloaddition of **1** by a biradical coupling pathway. Because **2** and **3** do not absorb light at >280 nm, they accumulate in the reaction mixture.

In earlier reviews of intermolecular photocycloaddition reactions [1,2], it was suggested that benzene derivatives and alkenes bearing either electron-releasing or electron-withdrawing substituents favor reaction by [2 + 2] photocycloadditon (*ortho*) pathways, whereas relatively simple alkenes and arenes undergo [3 + 2] photocycloaddition (*meta*) process. The observation made in the current study that photoreaction of **1h** (R = H, n = 4) produce only **3h** and not **4h** is in good agreement with the early suggestions. However, it is unclear why photoreactions of **1e-g** (R = H, n = 1-3) are inefficient in contrast to that of **1h**, although it is possible that steric repulsion might interfere with close approach of reaction centers.

The observed stereochemistry of **2** and **3** suggests that three important factors are at work in these photochemical reactions (Scheme 4). First, all photoproducts formed in these processes have a *cis*-relationship at the ring fusion formed by formation of bonds to the alkene carbons (H_a, H_b). This result, is consistent with observations made in studies of photoreactions of benzene derivatives with cycloalkenes [7,15,18,19] and is likely caused by a steric driven retention of the alkene *cis*-configuration and the higher proportion of reactions via excited singlet rather than triplet states. Second, the *trans*-orientation between benzylic hydrogen H_c and H_a, observed in the products of these processes, suggests that an *exo* mode of intramolecular addition is preferred over the corresponding *endo* mode. This preference is likely guided by steric hindrance rather orbital overlap interactions. This *exo*-selectivity is consistent with observations made in studies of photoreactions of cycloalkene linked benzenes **5** [24], although intermolecular version of this process often give both *exo* and *endo* products [7,15,18,19,21]. Finally, photoreactions of **1a-b** generate diastereomers that have different relative configurations from that found in the product of reaction of **1d**. This difference is associated with the configuration of the stereogenic center in the product derived from the allylic carbon.

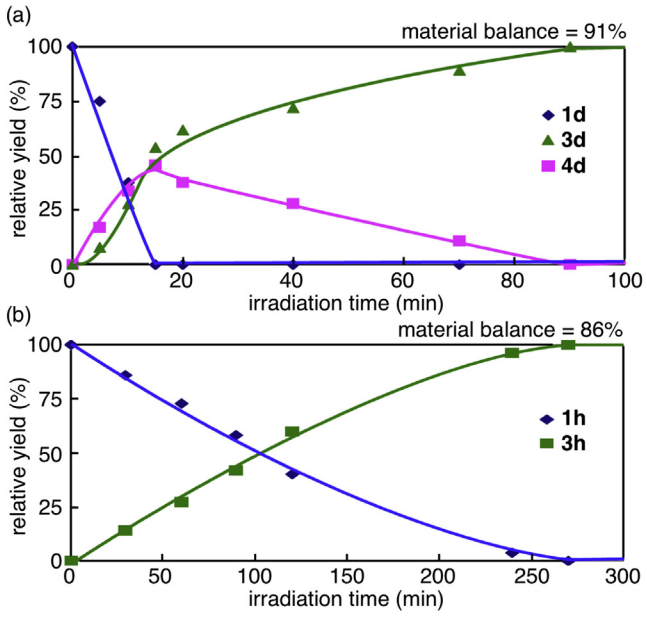
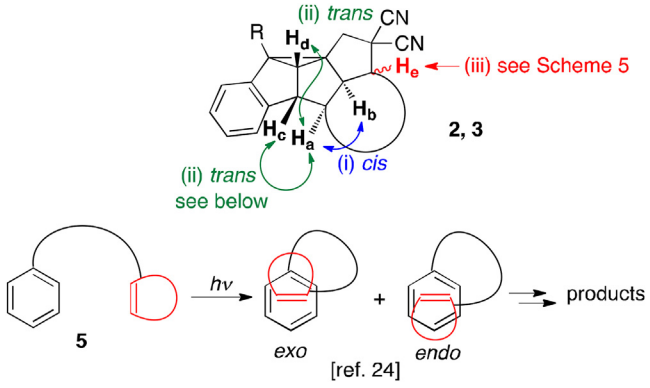


Fig. 2. Time-dependence of photoreactions of (a) **1d** and (b) **1h** in CD_3CN.

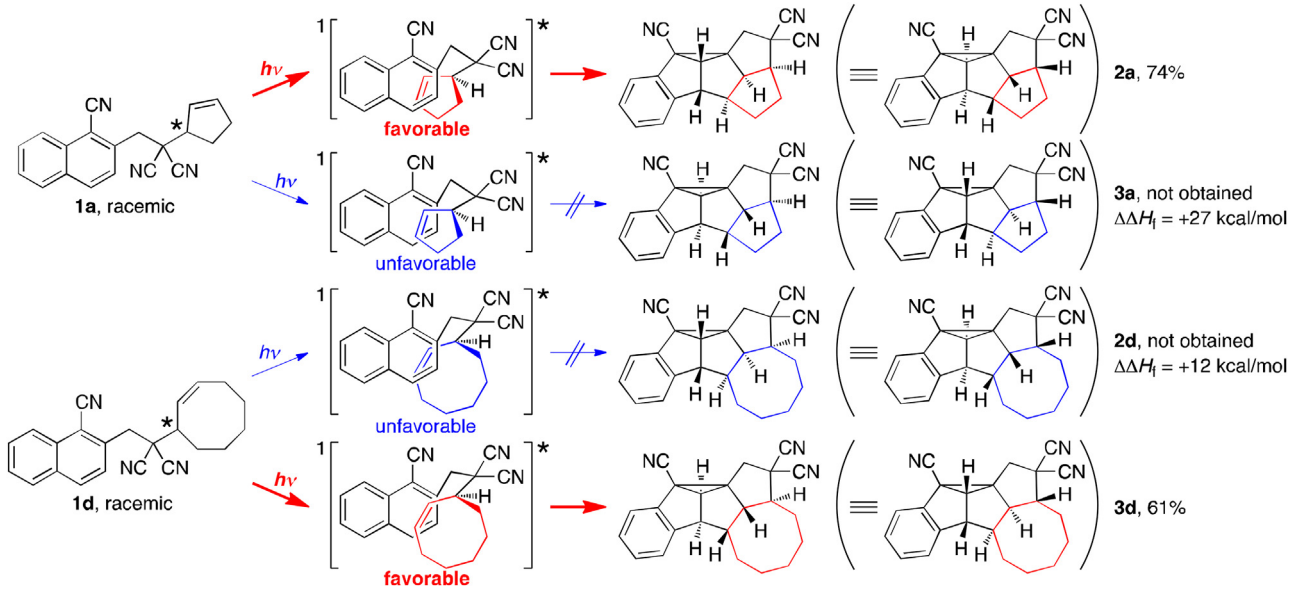


Scheme 4. Stereochemistry of products.

We believe that the difference lies in the facial selectivity in bonding of the cycloalkene to the 1-cyanonaphthalene moiety (Scheme 5). The results of theoretical calculations using HF/3-21G//PM3 indicate that products **2a** and **3d** are thermodynamically more stable than **3a** and **2d** ($\Delta\Delta H_f = 27$ and 12 kcal/mol), respectively. Therefore, it is anticipated that exciplexes that give rise to **2a** and **3d** are more stable than those that form **3a** and **2d**, respectively, owing to steric reason. (In Scheme 5, products in parentheses are enantiomers. We use racemic compounds, therefore, enantiomers are not distinguished, and we discuss only relative configurations.)

3. Conclusion

In this study, we investigated intramolecular photocycloaddition reactions of cycloalkene linked 1-cyanonaphthalenes and naphthalenes. The results show that in general these process lead to efficient and stereoselective production of pentacyclic products. In photoreactions of the 1-cyanonaphthalene-linked compounds (R = CN), 1,2-[2 + 2], photocycloadducts are initially formed and undergo cycloreversion to starting materials. This process is followed by less efficient 2,4-[3 + 2] photocycloaddition of the substrates to produce the observed pentacyclic products. Photoreactions of the linked naphthalenes bearing five to seven-membered cycloalkenes (**1e–g**) are sluggish but that bearing cyclooctene (**1h**) produces a pentacyclic product in high yield. The result of theoretical calculation show that the stereochemical outcomes of these reactions are governed by steric factors that guide stereoselective intramolecular exciplex formation. Various methods are available for the preparation of pentacyclic compounds by using thermal [55–66], photochemical [67–71] and transition-metal catalyzed reactions [72,73]. We believe that the photocycloaddition route described above is a significant addition to this list owing to the fact that processes are both efficient stereoselective, they take place in one-step and they utilize a clean energy source.



Scheme 5. Explanation of the diastereoselectivities of photoreactions of **1a** and **1d**.

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. THF was distilled from CaH_2 and then from Na/$Ph_2C{=}O$. ^1H 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. 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 were obtained using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Ka radiation. Structures were solved by using direct methods (SIR92) and expanded by using Fourier techniques. All calculations were performed using the Crystal Structure crystallographic software package. Theoretical calculations using HF/3-21G//PM3 were performed by using Spartan '04 software package for Windows.

4.2. Preparation of 1-Cyano-2-[2,2-dicyano-2-(cyclopent-2-en-1-yl) ethyl]naphthalene (**1a**)

To a stirred CCl_4 (20 mL) solution of cyclopentene (2.94 g, 43.1 mmol) were added *N*-bromosuccinimide (8.06 g, 45.3 mmol) and benzoyl peroxide (catalytic amount). The solution was stirred at reflux for 1 h. The formed solid was removed by filtration. The filtrate was concentrated in vacuo to give 3-bromocyclopentene, which was used to further reaction without purification.

To a stirred suspension of NaH (60% in mineral oil, 2.60 g, 65.0 mmol) in THF (10 mL) was slowly added a THF (5 mL) solution of malononitrile (5.70 g, 86.2 mmol) at 0 °C under argon atmosphere. The suspension was stirred for 1 h at room temperature. A THF (5 mL) solution of 3-bromocyclopentene was slowly added at 0 °C and the solution was stirred for 2 h at room temperature. Et_2O and brine were added and the organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) to give 3-(dicyanomethyl)cyclopentene (0.889 g, 6.73 mmol, 16% yield). Black liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 1.55–1.90 (m, 1H), 2.27–2.52 (m, 2H), 2.55–2.68 (m, 1H), 3.35–3.43 (m, 1H), 3.66 (d, J = 6.0 Hz, 1H), 5.70–5.74 (m, 1H), 6.12–6.16 (m, 1H) ppm.

To a stirred CCl_4 (60 mL) solution of 2-methylnaphthalene (20.1 g, 141 mmol), Fe powder (catalytic amount) and I_2 (catalytic amount) were slowly added a CCl_4 (10 mL) solution of Br_2 (22.5 g, 7.2 mL, 141 mmol) at 0 °C. The solution was stirred for 3 h. Sat $Na_2S_2O_3$ aq was added. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane) to give 1-bromo-2-methylnaphthalene (29.3 g, 133 mmol, 94% yield). Brown liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 2.58 (s, 3H), 7.26–8.24 (m, 6H) ppm.

A mixture of 1-bromo-2-methylnaphthalene (20.2 g, 91.3 mmol), CuCN (22.6 g, 252 mmol), *N*-methylpyrrolidone (50 mL) was stirred at 200 °C for 40 min. After the mixture was cooled to room temperature, 25% NH_3 aq (40 mL) and $CHCl_3$ were added. The separated organic layer was concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 1-cyano-2-methylnaphthalene (11.9 g, 71.1 mmol, 79% yield). Colorless solid; ^1H NMR (300 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.25–8.21 (m, 6H) ppm.

To a stirred CCl_4 solution (50 mL) of 1-cyano-2-methylnaphthalene (8.10 g, 48.4 mmol) was added *N*-bromosuccinimide (10.1 g, 56.7 mmol) and benzoyl peroxide (catalytic amount), and the solution was stirred at reflux for 4 h. The solid was removed by filtration. The filtrate was concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 2-bromomethyl-1-cyanonaphthalene (10.1 g, 41.0 mmol, 85% yield). Colorless solid; ^1H NMR (300 MHz, $CDCl_3$) δ 4.85 (s, 2H), 7.49–8.21 (m, 6H) ppm.

To a stirred suspension of NaH (60% in mineral oil, 88 mg, 2.2 mmol) in THF (30 mL) was slowly added THF (10 mL) solution of 3-(dicyanomethyl)cyclopentene (250 mg, 1.89 mmol) at 0 °C under argon atmosphere. The solution was stirred at room temperature for 1 h. To the solution was added a THF (20 mL) solution of 2-bromomethyl-1-cyanonaphthalene (492 mg, 2.0 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. Brine and Et_2O were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane:AcOEt = 5:1) followed by recycling preparative HPLC (GPC, eluent; $CHCl_3$) to give 1-cyano-2-[2,2-dicyano-2-(cyclopent-2-en-1-yl)ethyl]naphthalene (**1a**, 329 mg, 1.11 mmol, 61% yield). Colorless solid; mp 135.5–137.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.07–2.16 (m, 1H), 2.37–2.56 (m, 2H), 2.65–2.76 (m, 1H), 3.46–3.52 (m, 1H), 3.58 (d, J = 14.1 Hz, 1H), 3.72 (d, J = 14.1 Hz, 1H), 5.87–5.91 (m, 1H), 6.22–6.26 (m, 1H), 7.63–7.76 (m, 3H), 7.94 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.28 (dd, J = 8.4, 0.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 32.7, 40.0, 43.8, 54.1, 111.9, 114.3, 114.5, 116.3, 125.7, 126.1, 126.5, 128.1, 128.5, 129.2, 132.5, 132.6, 133.5, 136.5, 138.7 ppm; IR (KBr) ν 2219, 2246 cm^{-1}; MS (EI) m/z 297 (M^+).

4.3. Preparation of 1-Cyano-2-[2,2-dicyano-2-(cyclohex-2-en-1-yl) ethyl]naphthalene (**1b**)

To a stirred CCl_4 solution (20 mL) of cyclohexene (5.18 g, 63.1 mmol) were added *N*-bromosuccinimide (11.4 g, 63.8 mmol) and benzoyl peroxide (catalytic amount), and the solution was stirred at reflux for 3 h. The solid was removed by filtration. The filtrate was concentrated in vacuo to give 3-bromocyclohexene, which was used in the further reaction without purification.

To a stirred suspension of NaH (60% in mineral oil, 2.68 g, 67.0 mmol) in THF (10 mL) was slowly added a THF (5 mL) solution of malononitrile (4.02 g, 60.9 mmol) at 0 °C under argon astosphere. The suspension was stirred for 1 h at room temperature. A THF (5 mL) solution of 3-bromocyclohexene was slowly added at 0 °C, and the solution was stirred for 3 h at room temperature. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) to give 3-(dicyanomethyl)cyclohexene (1.33 g, 9.06 mmol, 15% yield). Black oil; ^1H NMR (300 MHz, $CDCl_3$) δ 1.58–1.63 (m, 2H), 1.86 (m, 1H), 2.07–2.13 (m, 3H), 2.80–2.87 (m, 1H), 3.64 (d, J = 3.3 Hz, 1H), 5.65 (m, 1H), 6.07 (m, 1H) ppm.

Reaction of 2-bromomethyl-1-cyanonaphthalene with 3-(dicyanomethyl)cyclohexene was carried out in a manner that is similar to that used for the preparation of **1a** to give 1-cyano-2-[2,2-dicyano-2-(cyclohex-2-en-1-yl)ethyl]naphthalene (**1b**) in 77% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 1.56–1.82 (m, 2H), 1.96–2.06 (m, 1H), 2.10–2.18 (m, 2H), 2.23–2.33 (m, 1H), 2.92–3.01 (m, 1H), 3.66 (s, 2H), 5.84–5.91 (m, 1H), 6.15–6.23 (m, 1H), 7.62–7.76

(m, 3H), 7.94 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.28 (d, J = 7.8 Hz, 1H) ppm; IR (KBr) ν 2220 cm^{-1}; MS (EI) m/z (relative intensity) 81 (100), 166 (97), 311 (16, M^+).

4.4. Preparation of 1-Cyano-2-[2,2-dicyano-2-(cyclohept-2-en-1-yl) ethyl]naphthalene (**1c**)

To a stirred CCl_4 solution (50 mL) of cycloheptene (3.88 g, 40.4 mmol) were added *N*-bromosuccinimide (7.25 g, 40.7 mmol) and benzoyl peroxide (catalytic amount), and the solution was stirred under reflux for 1 h. The solid was removed by filtration. The filtrate was concentrated in vacuo to give 3-bromocycloheptene, which was used in the further reaction without purification.

To a stirred suspension of NaH (60% in mineral oil, 1.94 g, 48.4 mmol) in THF (30 mL) was slowly added a THF (10 mL) solution of malononitrile (3.17 g, 47.9 mmol) at 0 °C under argon atmosphere. The suspension was stirred for 40 min at room temperature. A THF (10 mL) solution of 3-bromocycloheptene was slowly added at 0 °C, and the solution was stirred for 2 h at room temperature. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) to give 3-(dicyanomethyl)cycloheptene (3.39 g, 21.2 mmol, 53% yield). Pale yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35–2.44 (m, 8H), 2.95 (s, 1H), 3.70 (d, J = 6.0 Hz, 1H), 5.55–5.61 (m, 1H), 6.02–6.11 (m, 1H) ppm.

To a stirred suspension of NaH (60% in mineral oil, 0.433 g, 10.8 mmol) in THF (20 mL) was slowly added a THF (10 mL) solution of 3-(dicyanomethyl)cycloheptene (1.46 g, 9.11 mmol) at 0 °C under argon atmosphere, and the solution was stirred for 40 min at room temperature. To the solution was slowly added a THF (10 mL) solution of 2-bromomethyl-1-cyanonaphthalene (2.56 g, 10.4 mmol, see preparation of **1a**) at 0 °C, and the solution was stirred for 2 h at room temperature. Brine and Et_2O were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 1-cyano-2-[2,2-dicyano-2-(cyclohept-2-en-1-yl)ethyl]naphthalene (**1c**, 0.595 g, 1.83 mmol, 20% yield). Colorless needle; mp 168–170 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.38–1.46 (m, 1H), 1.65–1.83 (m, 3H), 2.12–2.37 (m, 4H), 3.04–3.06 (m, 1H), 3.61 (d, J = 14.1 Hz, 1H), 3.73 (d, J = 14.1 Hz, 1H), 5.89–5.94 (m, 1H), 6.15–6.23 (m, 1H), 7.63–7.77 (m, 3H), 7.96 (d, J = 8.1 Hz, 1H) 8.14 (d, J = 8.7 Hz, 1H), 8.29 (d, J = 9.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 28.3, 30.15, 30.22, 39.3, 44.2, 47.1, 112.0, 114.3, 114.7, 116.3, 125.7, 126.5, 128.0, 128.1, 128.5, 129.2, 132.5, 132.6, 133.5, 136.4, 136.5 ppm; MS (EI) m/z (relative intensity) 142 (100, $C_{11}H_{10}$), 325 (19, M^+); IR (KBr) ν 2222 cm^{-1}.

4.5. Preparation of 1-Cyano-2-[2,2-dicyano-2-(cyclooct-2-en-1-yl) ethyl]naphthalene (**1d**)

To a stirred CCl_4 solution (150 mL) of cyclooctene (8.82 g, 80.0 mmol) were added *N*-bromosuccinimide (15.1 g, 84.8 mmol) and benzoyl peroxide (catalytic amount), and the solution was stirred under reflux for 3 h. The solid was removed by filtration. The filtrate was concentrated in vacuo to give 3-bromocyclooctene (13.92 g, 73.6 mmol, 92% yield), which was used in the further reaction without purification. Brown oil; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29–1.46 (m, 2H), 1.48–1.72 (m, 4H), 1.94–2.29 (m, 4H), 4.95 (m, 1H), 5.60 (ddd, J = 6.2, 1.5, 1.2 Hz, 1H), 5.76 (dd, J = 6.9, 1.5 Hz, 1H).

To a stirred suspension of NaH (60% in mineral oil, 2.21 g, 55.0 mmol) in THF (50 mL) was slowly added a THF (20 mL) solution of malononitrile (3.95 g, 60.0 mmol) at 0 °C under argon atmosphere. The suspension was stirred for 40 min at room temperature. A THF (20 mL) solution of 3-bromocyclooctene (5.67 g, 30.0 mmol) was slowly added at −78 °C, and the solution was stirred for 30 min at −78 °C then for 1 h at room temperature. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane: AcOEt = 5:1) followed by distillation under reduced pressure to give 3-(dicyanomethyl)cyclooctene (1.43 g, 8.21 mmol, 27% yield). Dark brown oil; bp 152 °C/6 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85–2.21 (m, 10H), 3.18 (m, 1H), 3.70 (d, J = 5.7 Hz, 1H), 5.41 (dd, J = 10.5, 8.7 Hz, 1H), 6.00 (ddd, J = 9.9, 8.7, 8.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 26.5, 27.0, 28.7, 29.1, 33.8, 38.5, 112.1 (2C), 125.9, 134.6 ppm; IR (neat) ν 723, 758, 1449, 2254, 2857, 3018 cm^{-1}; MS (EI) m/z (relative intensity) 67 (100), 109 (21), 174 (3, M^+).

To a stirred suspension of NaH (60% in mineral oil, 0.178 g, 4.44 mmol) in THF (50 mL) was slowly added THF (20 mL) solution of 3-(dicyanomethyl)cyclooctene (0.516 g, 2.96 mmol) at 0 °C under argon atmosphere. The solution was stirred at 0 °C for 1 h. To the solution was added a THF (20 mL) solution of 2-bromomethyl-1-cyanonaphthalene (1.25 g, 5.07 mmol, see preparation of **1a**) at 0 °C, and the solution was stirred at room temperature for 1 h. Brine and benzene were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; benzene) gave 1-cyano-2-[2,2-dicyano-2-(cyclooct-2-en-1-yl)ethyl]naphthalene (**1d**, 0.632 g, 1.86 mmol, 63% yield) Colorless blocks; mp 182–184 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35–1.46 (m, 2H), 1.55–1.81 (m, 5H), 2.18–2.29 (m, 3H), 3.20 (m, 1H), 3.54 (d, J = 14.1 Hz, 1H), 3.77 (d, J = 14.1 Hz, 1H), 5.62 (dd, J = 10.4, 9.3 Hz, 1H), 6.12 (ddd, J = 10.4, 8.7, 8.5 Hz, 1H), 7.63–7.77 (m, 3H), 7.95 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 8.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 27.0, 27.5, 29.2, 33.0, 41.1, 43.8, 44.2, 112.0, 113.9, 114.7, 116.2, 124.7, 125.7, 126.5, 128.0, 128.4, 129.2, 132.4, 132.6, 133.4, 135.7, 136.5 ppm; IR (KBr) ν 756, 835, 1415, 2218, 2857, 2931 cm^{-1}; MS (EI) m/z (relative intensity) 67 (100), 109 (26), 166 (86), 231 (20), 339 (6, M^+); Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.39; H, 6.24; N, 12.38. Found: C, 81.38; H, 6.23; N, 12.21.

4.6. Preparation of 2-[2,2-Dicyano-2-(cyclopent-2-en-1-yl)ethyl] naphthalene (**1e**)

To a stirred CCl_4 (70 mL) solution of 2-methylnaphthalene (20.2 g, 142 mmol) were added *N*-bromosuccinimide (26.9 g, 151 mmol) and benzoyl peroxide (catalytic amount), and the solution was stirred for 2 h under reflux. The solid was removed by filtration. The filtrate was concentrated in vacuo to give 2-(bromomethyl)naphthalene (31.2 g, 141 mmol, 99% yield), which was used in the further reaction without purification. Brown solid, ^1H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2H), 7.26–7.52 (m, 3H), 7.80–7.84 (m, 4H) ppm.

To a stirred suspension of NaH (60% in mineral oil, 0.233 g, 5.83 mmol) in THF (20 mL) was slowly added a THF (5 mL) solution of 3-(dicyanomethyl)cyclopentene (0.789 g, 5.97 mmol, see preparation of **1a**) at 0 °C under argon atmosphere, and the suspension was stirred at room temperature for 30 min. To the solution was slowly added a THF (5 mL) solution of 2-(bromomethyl)naphthalene (1.34 g, 6.06 mmol) at 0 °C, and the solution was stirred for 2 h at room temperature. Et_2O and brine were added. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 2-[2,2-dicyano-2-(cyclopent-2-en-1-yl)ethyl]naphthalene (**1e**, 0.910 g, 3.34 mmol, 56% yield). Pale yellow solid; mp 108–109 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.06 (m, 1H), 2.32–2.43 (m, 1H), 2.47–2.51 (m, 1H), 2.66–2.68 (m, 1H), 3.35–3.36 (m, 3H), 5.82–5.86 (m, 1H), 6.19–6.23 (m, 1H), 7.48–7.53 (m, 3H), 7.86–7.89

(m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7, 32.6, 41.7, 41.7, 53.3, 76.7, 77.1, 77.5, 126.4, 126.5, 126.6, 127.4, 127.7, 128.0, 128.7, 129.5, 129.7, 138.1 ppm; IR (KBr) ν 2246 cm^{-1}; MS (EI) *m/z* (relative intensity) 142 (100, $C_{11}H_{10}$), 272 (16, M^+).

4.7. Preparation of 2-[2,2-Dicyano-2-(cyclohex-2-en-1-yl)ethyl] naphthalene (**1f**)

To a stirred suspension of NaH (60% in mineral oil, 0.246 g, 10.3 mmol) in THF (10 mL) was slowly added a THF (5 mL) solution of 3-(dicyanomethyl)cyclohexene (1.00 g, 6.85 mmol, see preparation of **1b**) at 0 °C under argon atmosphere, and the solution was stirred for 1 h at room temperature. To the solution was slowly added a THF (5 mL) solution of 2-(bromomethyl)naphthalene (1.51 g, 6.84 mmol, see preparation of **1e**) at 0 °C, and the solution was stirred for 3 h at room temperature. Brine and Et_2O were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 2-[2,2-dicyano-2-(cyclohex-2-en-1-yl)ethyl]naphthalene (**1f**, 1.01 g, 3.51 mmol, 51% yield). Pale yellow solid; mp 123–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52–1.72 (m, 2H), 1.98 (m, 1H), 2.12 (m, 2H), 2.19 (m, 1H), 2.82 (m, 1H), 3.38 (s, 2H), 5.84 (m, 1H), 6.16 (m, 1H), 7.49–7.53 (m, 3H), 7.84–7.90 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 25.0, 26.0, 40.5, 42.3, 44.9, 115.0, 122.5, 126.5, 126.6, 127.4, 127.7, 128.0, 128.7, 129.6, 129.8, 133.1, 132.2, 134.4 ppm; IR (KBr) ν 2243 cm^{-1}; MS (EI) *m/z* (relative intensity) 142 (100, $C_{11}H_{10}$), 286 (12, M^+).

4.8. Preparation of 2-[2,2-Dicyano-2-(cyclohept-2-en-1-yl)ethyl] naphthalene (**1g**)

To a stirred suspension of NaH (60% in mineral oil, 0.462 g, 11.6 mmol) in THF (20 mL) was slowly added a THF (5 mL) solution of 3-(dicyanomethyl)cycloheptene (1.51 g, 9.44 mmol, see preparation of **1c**) at 0 °C under argon atmosphere, and the solution was stirred for 50 min at room temperature. To the solution was slowly added a THF (5 mL) solution of 2-(bromomethyl)naphthalene (2.28 g, 10.3 mmol, see preparation of **1e**) at 0 °C, and the solution was stirred for 2 h at room temperature. Brine and Et_2O were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; hexane-AcOEt) followed by recrystallization from EtOH to give 2-[2,2-dicyano-2-(cyclohept-2-en-1-yl)ethyl]naphthalene (**1g**, 1.64 g, 5.46 mmol, 58% yield). Colorless solid; mp 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35–1.42 (m, 1H), 1.62–1.73 (m, 2H), 2.07–2.16 (m, 2H), 2.23–2.33 (m, 1H), 2.84 (m, 1H), 3.40 (dd, *J* = 4.2, 4.1 Hz, 2H), 5.84–5.89 (m, 1H), 6.12–6.21 (m, 1H), 7.64–7.53 (m, 3H) 7.84–7.88 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 28.3, 30.1, 30.3, 40.9, 44.6, 45.7, 115.0, 115.2, 126.5, 126.6, 127.5, 127.7, 128.0, 128.6, 128.7, 129.5, 129.7, 133.1, 133.2, 135.9 ppm; IR (KBr) ν 2245 cm^{-1}; MS (EI) *m/z* (relative intensity) 142 (100, $C_{11}H_{10}$), 300 (13, M^+).

4.9. Preparation of 2-[2,2-Dicyano-2-(cyclooct-2-en-1-yl)ethyl] naphthalene (**1h**)

To a stirred suspension of NaH (60% in mineral oil, 0.678 g, 17.0 mmol) in THF (7 mL) was added 3-(dicyanomethyl)cyclooctene (0.516 g, 2.96 mmol, see preparation of **1d**) at 0 °C under argon atmosphere. The solution was stirred at 0 °C for 30 min. To the solution was added a THF (5 mL) solution of 2-(bromomethyl) naphthalene (2.50 g, 11.3 mmol, see preparation of **1e**) at 0 °C, and the solution was stirred at room temperature for 1.5 h. Brine and Et_2O were added. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to silica gel column chromatography (eluent; benzene) to give 2-[2,2-dicyano-2-(cyclooct-2-en-1-yl)ethyl]naphthalene (**1h**, 1.52 g, 4.83 mmol, 43% yield). Colorless powder; mp 154–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24–1.37 (m, 2H), 1.51–1.70 (m, 4H), 2.01 (m, 1H), 2.19 (m, 1H), 2.95 (m, 1H), 3.30 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 5.57 (dd, *J* = 10.2, 10.2 Hz, 1H), 6.11 (ddd, *J* = 9.3, 9.0, 8.4 Hz, 1H), 7.49–7.52 (m, 3H), 7.81–7.87 (m, 4H) ppm; 25.2, 27.0, 27.6, 29.3, 32.9, 42.0, 42.1, 44.0, 114.8, 115.2, 125.4, 126.4, 126.5, 127.6, 127.7, 127.9, 128.5, 129.4, 129.7, 133.0, 133.1, 135.1 ppm; IR (KBr) ν 758, 824, 1149, 2245, 2857, 2938 cm^{-1}; MS (EI) *m/z* (relative intensity) 67 (20), 141 (100), 142 (21), 314 (4, M^+); Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.94; H, 6.93; N, 8.90.

4.10. General procedure for photoreaction

A dry acetonitrile solution containing the substrate (5–30 mM, see Table 1) 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 use of circulated cooling water during irradiation.

4.10.1. (2aS*,4aS*,4bS*,8bS*,8cR*,8dR*,8eS*)-3,4,4a,4b,8d,8e-Hexahydrobenzo[f]cyclopropa[cd]pentaleno[1,6-ab]pentalene-2,2,8b (1H,2aH)-tricarbonitrile (**2a**)

Colorless solid; mp 189–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79–2.17 (m, 4H), 2.37–2.45 (m, 1H), 2.74–2.81 (m, 2H), 3.09 (d, *J* = 14.1 Hz, 1H), 3.22–3.27 (m, 1H), 3.41 (d, *J* = 5.0 Hz, 1H), 3.85 (d, *J* = 5.1 Hz, 1H), 7.06–7.09 (m, 1H), 7.19–7.28 (m, 2H), 7.41–7.44 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 25.8, 35.0, 37.4, 37.7, 41.7, 49.2, 50.1, 51.3, 54.6, 64.8, 114.6, 115.1, 117.0, 123.8, 125.7, 127.4, 128.1, 135.9, 142.5 ppm; IR (KBr) ν 2232, 2251 cm^{-1}; MS (EI) *m/z* 297 (M^+).

4.10.2. (2aS*,5aS*,5bS*,9bS*,9cR*,9dR*,9eS*)-4,5,5a,5b,9d,9e-Hexahydro-3H-benzo[4,5]cyclopropa[1,6]pentaleno[1,2,3-cd]indene-2,2,9b(1H,2aH)-tricarbonitrile (**2b**)

Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01–1.22 (m, 3H), 1.79–1.88 (m, 1H), 1.96–2.08 (m, 2H), 2.10–2.20 (m, 1H), 2.40 (t, *J* = 6.7 Hz, 1H), 2.66–2.72 (m, 1H), 2.87 (s, 2H), 3.30 (d, *J* = 4.9 Hz, 1H), 3.76 (d, *J* = 5.1 Hz, 1H), 7.04–7.07 (m, 1H), 7.21–7.32 (m, 2H), 7.48–7.50 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 26.3, 29.4, 35.4, 38.5, 42.3, 43.4, 44.8, 47.1, 50.4, 53.6, 60.4, 113.0, 115.3, 117.1, 123.5, 123.8, 128.1, 128.3, 135.2, 144.9 ppm; IR (KBr) ν 2231 cm^{-1}; MS (EI) *m/z* (relative intensity) 141 (100), 311 (8, M^+).

4.10.3. (2aS*,6aS*,6bS*,10bS*,10cR*,10dR*,10eS*)-5,6,6a,6b,10d,10e-Hexahydrobenzo[4,5]cyclopropa[1,6]pentaleno[1,2,3-cd]azulene-2,2,10b(1H,2aH)-tricarbonitrile (**2c**)

Colorless block; mp 251–253 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39–1.53 (m, 2H), 1.75–2.20 (m, 7H), 2.39 (dd, *J* = 5.7, 3.6 Hz, 1H), 2.78–2.85 (m, 3H), 3.44 (d, *J* = 5.1 Hz, 1H), 3.63 (d, *J* = 5.4 Hz, 1H), 7.07–7.10 (m, 1H), 7.21–7.31 (m, 2H), 7.44–7.47 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 26.1, 27.1, 30.7, 40.7, 41.0, 40.7, 48.0, 51.97, 52.02, 60.3, 60.8, 114.9, 115.5, 117.0, 123.6, 123.7, 128.0, 128.3, 135.4, 145.7 ppm; IR (KBr) ν 2233 cm^{-1}; MS (EI) *m/z* (relative intensity) 142 (100, $C_{11}H_{10}$), 325 (19, M^+).

4.10.4. (2aR*,6aS*,6bS*,10bS*,10cR*,10dR*,10eS*)-5,6,6a,6b,10d,10e-Hexahydrobenzo[4,5]cyclopropa[1,6]pentaleno[1,2,3-cd]azulene-2,2,10b(1H,2aH)-tricarbonitrile (**3c**)

Colorless block; mp 255–257 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30–1.62 (m, 3H), 1.66–1.89 (m, 4H), 2.04–2.19 (m, 2H), 2.61–2.79 (m, 3H), 3.02 (d, *J* = 14.7 Hz, 1H), 3.25 (d, *J* = 5.1 Hz, 1H), 3.67 (d, *J* = 5.1 Hz, 1H), 7.04–7.08 (m, 1H), 7.19–7.28 (m, 2H), 7.44–7.47 (m,

1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 27.4, 28.5, 31.3, 32.5, 40.5, 42.0, 47.9, 52.3, 53.2, 57.5, 60.0, 113.9, 114.8 (2C), 117.7, 122.8, 123.9, 127.4, 128.5, 133.8, 149.6 ppm; IR (KBr) ν 2231 cm^{-1}; MS (EI) m/z (relative intensity) 142 (100, $C_{11}H_{10}$), 325 (7, M^+).

4.10.5. (4bS,4cS*,10R*,10aR*,10cS*,10dS*)-4c,5,6,7,8,9,10,10a,10c,10d-Decahydro-4bH-10,10b-ethanobenzo[a]cycloocta[f]cyclopropa[cd] pentalene-10c,12,12-tricarbonitrile (**3d**)*

Colorless needle; mp 247–249 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–2.15 (m, 13H), 2.71–2.79 (m, 1H), 2.95 (d, J = 14.1 Hz, 1H), 3.23 (d, J = 6.0 Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 7.10 (d, J = 6.6 Hz, 1H), 7.23–7.32 (m, 2H), 7.48 (d, J = 8.1 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 26.0, 29.1, 30.9, 32.4, 35.4, 41.2, 42.9, 46.3, 49.6, 50.0, 51.6, 60.3, 63.7, 113.7, 114.4, 117.1, 123.6, 123.7, 128.0, 128.3, 134.7, 146.6 ppm; IR (KBr) ν 771, 944, 1459, 1477, 2230, 2253, 2901, 2931 cm^{-1}; MS (EI) m/z (relative intensity) 141 (100), 339 (2, M^+).

4.10.6. (4bS,4cS*,10R*,10aR*,10cS*,10dS*)-4c,5,6,7,8,9,10,10a,10c,10d-Decahydro-4bH-10,10b-ethanobenzo[a]cycloocta[f]cyclopropa[cd] pentalene-12,12-dicarbonitrile (**3h**)*

Colorless needle; mp 183–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10–2.03 (m, 13H), 2.48–2.73 (m, 4H), 3.48 (d, J = 4.8 Hz, 1H), 7.03–7.28 (m, 3H), 7.31 (d, J = 1.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.2, 26.2, 29.3, 31.2, 32.7, 39.4, 41.0, 43.1, 43.9, 44.4, 49.0, 49.7, 60.7, 64.0, 114.7, 115.4, 123.1, 124.0, 126.1, 126.8, 140.8, 147.7 ppm; IR (KBr) ν 747, 934, 1458, 1473, 2250, 2911, 2934 cm^{-1}; MS (EI) m/z (relative intensity) 67 (23), 141 (100), 314 (6, M^+).

*4.10.7. 7,8,9,10,11,12,12a,12b-Octahydro-6bH-6a,7-ethanocycloocta [3,4]cyclobuta[1,2-a]naphthalene-12b,13,13-tricarbonitrile (**4d**)*

Colorless plates; mp 214–216 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06–2.14 (m, 13H), 2.53 (s, 1H), 2.58 (s, 1H), 5.83 (d, J = 9.9 Hz, 1H), 6.47 (d, J = 9.9 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.23–7.30 (m, 2H), 7.48 (d, J = 8.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 24.2, 24.6, 26.7, 30.6, 42.8, 45.1, 48.6, 48.7, 49.2, 52.7, 59.5, 114.5, 114.6, 120.0, 125.9, 126.1, 128.3, 128.6, 128.9, 129.2, 129.4, 129.6 ppm; IR (KBr) ν 793, 1450, 1459, 2226, 2251, 2856, 2934 cm^{-1}; MS (EI) m/z (relative intensity) 58 (13), 67 (100), 81 (13), 109 (26), 166 (43), 339 (4, M^+).

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 and 26410049 to K. M., 20550049, 23550047, and 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, A-STEP (Adaptable and Seamless Technology Transfer Program through target-driven R&D, JST), and the Kanazawa University SAKIGAKE project.

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.2017.01.008.

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