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Intramolecular Photocycloaddition Reactions of Arylcyclopropane Tethered 1-Cyanonaphthalenes

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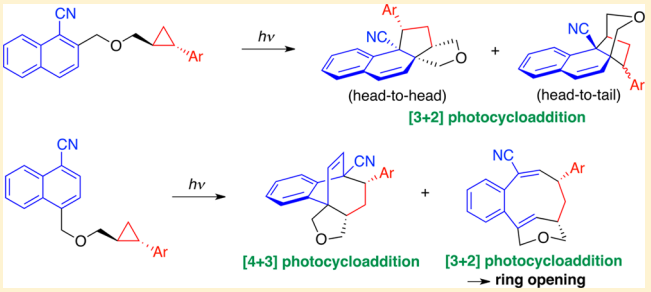
Supporting Information

ABSTRACT: Intramolecular photocycloaddition reactions of 1-cyanonaphthalenes bearing an arylcyclopropane containing side chain were investigated. Photoreactions of members of this family in which the arylcyclopropane moiety is bonded at the 2-position of the 1-cyanonaphthalene ring produce head-to-head and head-to-tail 1,2-[3+2] photocycloadducts. On the other hand, substances in this family containing an arylcyclopropane side chain linked to the 4-position of the cyanoarene ring undergo photoreactions to form [4+3] photocycloadducts along with novel nine-membered ring products, which are produced by photochemically induced 10π conrotatory ring opening of the initially formed intramolecular [3+2] cycloadducts. The results of solvent effects and fluorescence investigations along with those focusing on corresponding intermolecular photoreactions demonstrate that the photocycloadducts are formed predominantly through an intramolecular exciplex mechanism and that a photoinduced intramolecular electron transfer pathway via zwitterionic biradicals might be partly responsible for the process when CH_3CN is the solvent.

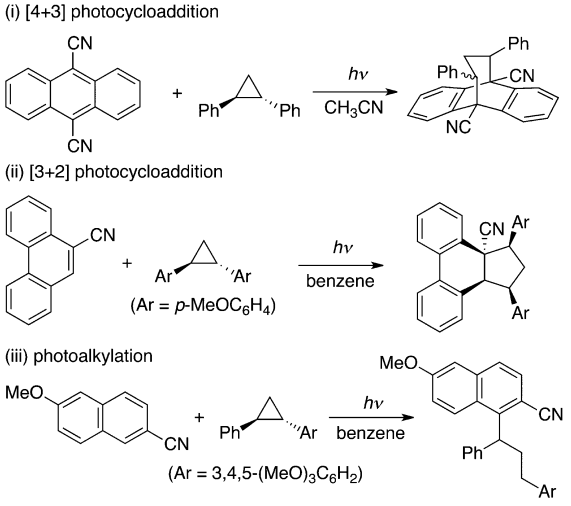


INTRODUCTION

Inter- and intramolecular photocycloaddition reactions of unsaturated compounds, such as alkenes, alkynes, allenes, and arenes, are useful for the preparation of various polycyclic compounds.[1] We envisioned that if cyclopropane derivatives could be utilized in place of unsaturated components, the photocycloaddition reactions would represent a new strategy for the synthesis of polycyclic compounds that contain fused cycloalkane rings. However, only a few examples of intermolecular photoreactions of alkenes with cyclopropanes have been described thus far[2] and even more sparse are reports of photoreactions of cyclopropanes with arenes (Scheme 1). The only processes of the latter type that have been uncovered are [4+3] photocycloaddition reactions of 9,10-dicyanoanthracene with 1,2-diarylcyclopropanes,[3] 1-amino-2-phenylcyclopropanes[4] and methylenecyclopropanes,[5] [3+2] photocycloadditions of 9-cyanophenanthrene with 1,2-dianisylcyclopropanes,[6] and regioselective photoalkylation of naphthalene with 1,2-diarylcyclopropanes.[7]

In contrast to their intermolecular counterparts, intramolecular reactions often take place with increased reaction rates, and high levels of regio- and stereoselectivity owing to close and pre-established locations of reactive centers. These phenomena have been considered in our recent design of linked alkene-naphthalene derivatives that undergo intramolecular photocycloaddition across the 1,3-position of the naphthalene ring[8] and linked alkene-pyrene systems that undergo site-selective intramolecular photocycloaddition reactions.[9] Up until now, no reports have appeared describing intramolecular photoreactions of arenes that contain tethered cyclopropane moieties. Based on the thought that processes of this type would be ideally suited to the construction of unique polycyclic compounds, we designed an investigation of photoreactions of model linked cyclopropane-arene systems.

Scheme 1. Photoreactions of Arenes with Cyclopropanes



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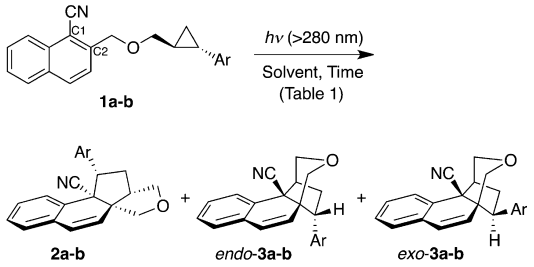
The results of this effort, which uncovered highly efficient photocycloaddition reactions that generate interesting polycyclic compounds, are described below.

RESULTS AND DISCUSSION

For the purposes of this exploratory study, linked 1-cyanonaphthalene-arylcyclopropane substrates **1a,b** (Scheme 2) were prepared and probed as candidates for intramolecular [3+2] photocycloaddition reactions. At the outset, we anticipated that the presence of the cyclopropane donor and cyanonaphthalene acceptor moieties in these substances would enable ready formation of intramolecular exciplexes, which typically participate as intermediates in photocycloaddition reactions.[10]

Scheme 2. Intramolecular [3+2] Photocycloaddition Reactions of 1a−b



In a test of our proposal, an argon purged CH_3CN solution containing 2-cyclopropane-linked 1-cyanonaphthalene **1a** (10 mM) in a Pyrex vessel (>280 nm) was irradiated by using a 300 W high pressure Hg lamp for 45 min (Table 1, entry 1). Silica gel column chromatography (eluent; hexane:EtOAc) of the crude reaction mixture followed by HPLC (GPC, eluent; $CHCl_3$) gave the intramolecular [3+2] photocycloadducts **2a**, *endo*-**3a**, and *exo*-**3a** as pure crystalline (from EtOH) substances in respective yields (by GLC) of 16, 7, and 19%. The structures of these photoproducts were determined by using X-ray crystallographic analysis (Figure 1). Regioisomeric products **2a** and **3a** arise in this process by respective head-to-head and head-to-tail [3+2] intramolecular cyloaddition of the cyclopropane group across the 1,2-position of the 1-cyanonaphthalene ring. Moreover, in contrast to **1a**, which has the phenyl group and methylene group in the linking chain *trans*-disposed, **2a** has these groups in a *cis*-orientation. *Endo*-**3a** and *exo*-**3a** are

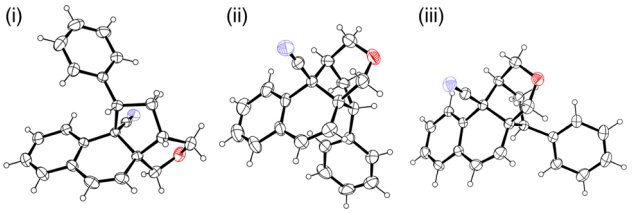


Figure 1. ORTEP plots of X-ray crystallographic data of (i) **2a**, (ii) *endo*-**3a**, and (iii) *exo*-**3a**.

stereoisomers that differ in the relative spatial orientations of the phenyl and methylene groups. Interestingly, photoreaction of the *p*-methoxy derivative **1b** leads to production of *endo*-**3b** and *exo*-**3b**, along with only a trace amount of **2b** (Entries 6−10). To the best of our knowledge, these are the first examples of intramolecular [3+2] photocycloaddition reactions of a tethered cyclopropane-arene system.

The effect of solvent on the photoreactions of **1a** and **1b** was examined by using CH_2Cl_2 and benzene. Although a change in solvent does not cause a remarkable difference in the product ratios arising in photoreaction of **1a**, it does impact the efficiency of the reaction which falls in the order of CH_3CN > CH_2Cl_2 > benzene (Entries 1−4). In contrast, photoreaction of the *p*-methoxy derivative **1b** proceeds most efficiently when benzene is the solvent, and the relative efficiencies follow the order benzene > CH_2Cl_2 > CH_3CN (Entries 6−10). The triplet sensitized photoreaction in the presence of benzophenone did not proceed (Entry 5).[11]

Next, we studied photoreactions of the 1-cyanonaphthalenes **4a,b** containing arylcyclopropanes linked at the 4-position of the naphthalene ring (Scheme 3). Photoreaction of **4a** (Ar =

Scheme 3. Intramolecular Photocycloaddition Reactions of 4a−b

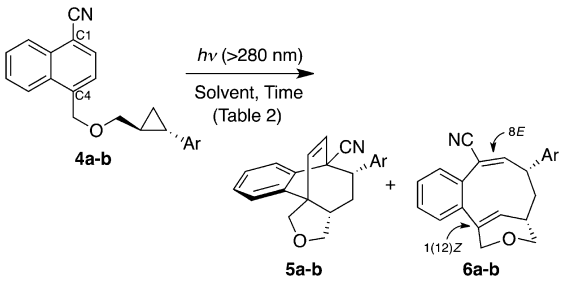


Table 1. Intramolecular [3+2] Photocycloaddition Reactions of 1a−b

				yields[a]/%			
entry	substrate	solvent and additive	time/h	**2**	*endo*-**3**	*exo*-**3**	recovery of **1**/%
1	**1a** (Ar = Ph)	CH_3CN	0.75	16	7	19	0
2	**1a** (Ar = Ph)	CH_2Cl_2	1.5	16	12	16	0
3	**1a** (Ar = Ph)	benzene	3.0	20	7	11	35
4	**1a** (Ar = Ph)	benzene	6.0	13	5	12	0
5	**1a** (Ar = Ph)	CD_3CN, $Ph_2C{=}O$[b]	12.0	0	0	0	99
6	**1b** (Ar = *p*-$MeOC_6H_4$)	CH_3CN	3.0	0	0	0	99
7	**1b** (Ar = *p*-$MeOC_6H_4$)	CH_2Cl_2	3.0	0	2	4	71
8	**1b** (Ar = *p*-$MeOC_6H_4$)	benzene	1.5	< 1	11	16	54
9	**1b** (Ar = *p*-$MeOC_6H_4$)	benzene	3.0	< 1	13	23	17
10	**1b** (Ar = *p*-$MeOC_6H_4$)	benzene	4.5	< 1	11	23	0

[a]Yields were determined by using GC with octadecane as an internal standard. [b]A solution (0.6 M of naphthalene in benzene) was used as the filter (>326 nm), 20 equiv of $Ph_2C{=}O$.

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Ph) was found to generate the intramolecular [4+3] photocycloadduct **5a** and the novel nine-membered ring containing compound **6a** (Table 2, Entries 1–5). Both products, whose

Table 2. Intramolecular Photocycloaddition Reactions of 4a–b

				yields[a]/%		
entry	substrate	solvent	time/h	5	6	recovery of 4/%
1	**4a** (Ar = Ph)	CH_3CN	0.67	7	11	8
2	**4a** (Ar = Ph)	CH_2Cl_2	0.83	8	13	6
3	**4a** (Ar = Ph)	benzene	0.5	4	7	68
4	**4a** (Ar = Ph)	benzene	1.33	11	14	17
5	**4a** (Ar = Ph)	benzene	2	15	11	2
6	**4b** (Ar = *p*-$MeOC_6H_4$)	CH_3CN	4	0	0	99
7	**4b** (Ar = *p*-$MeOC_6H_4$)	CH_2Cl_2	4	0	0	93
8	**4b** (Ar = *p*-$MeOC_6H_4$)	benzene	4	11	3	59
9	**4b** (Ar = *p*-$MeOC_6H_4$)	benzene	8	17	3	35
10	**4b** (Ar = *p*-$MeOC_6H_4$)	benzene	12	24	< 1	5

[a]Yields were determined by using ^{1}H NMR.

structures were determined by using X-ray crystallographic analysis (Figure 2), are formed as single stereoisomers having a

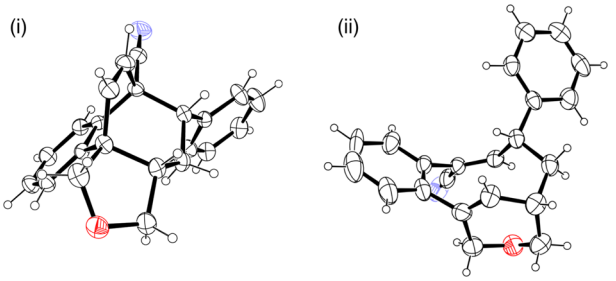

Figure 2. ORTEP plots of X-ray crystallographic data of (i) **5a** and (ii) **6a**.

cis-relationship between the phenyl group and the linking chain. In addition, the C=C double bonds in **6a** have 1(12)*Z* and 8*E* configurations.

The effect of solvent on photoreaction of **4a** displays a pattern that is similar to that of **1a**. Specifically, the product ratio is not influenced by solvent and the photoreaction proceeds more efficiently in CH_3CN. On the other hand, photoreaction of **4b** does not take place in CH_3CN and CH_2Cl_2, but it occurs efficiently in benzene. Finally, the **5b**/**6b** product ratio in reaction of **4b** is larger than that of **5a**/**6a** in reaction of **4a**.

Absorption and emission spectroscopic studies were conducted in order to gain information about the nature of the excited state involved in these reactions. UV absorption spectra of **1a,b** and **4a,b** (1×10^{-4} M in CH_2Cl_2) were measured and compared to those of 1-cyano-2-methylnaphthalene and 1-cyano-4-methylnaphthalene (Figure 3). Because the absorption maxima and molar extinction coefficients of **1a,b** and **4a,b** are similar to those of 1-cyano-2-methylnaphthalene and 1-cyano-4-methylnaphthalene, respectively, light absorption by the linked substrates takes place in the 1-

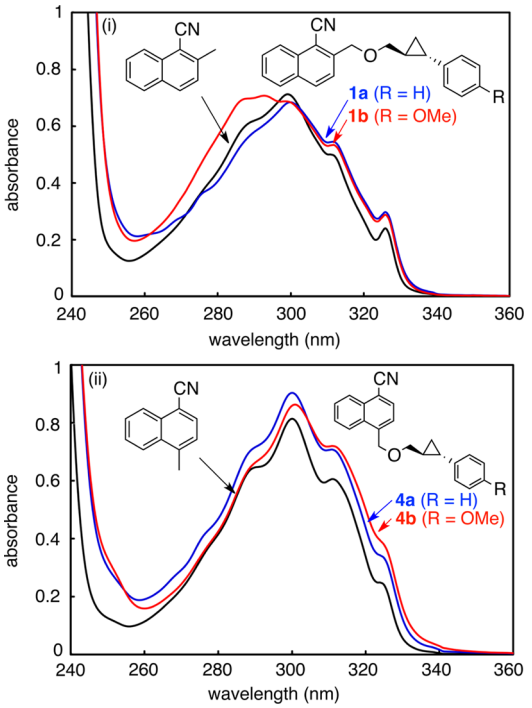

Figure 3. UV absorption spectra of 1×10^{-4} M CH_2Cl_2 solutions of (i) **1a,b** and 1-cyano-2-methylnaphthalene, and (ii) **4a,b** and 1-cyano-4-methylnaphthalene.

cyanonaphthalene chromophore. Inspection of the fluorescence spectra of CH_2Cl_2 solutions of **1a** and **4a** (Figure 4) showed that both substances display exclusive monomer emission from a localized excited 1-cyanonaphthalene fluorophore (320–380

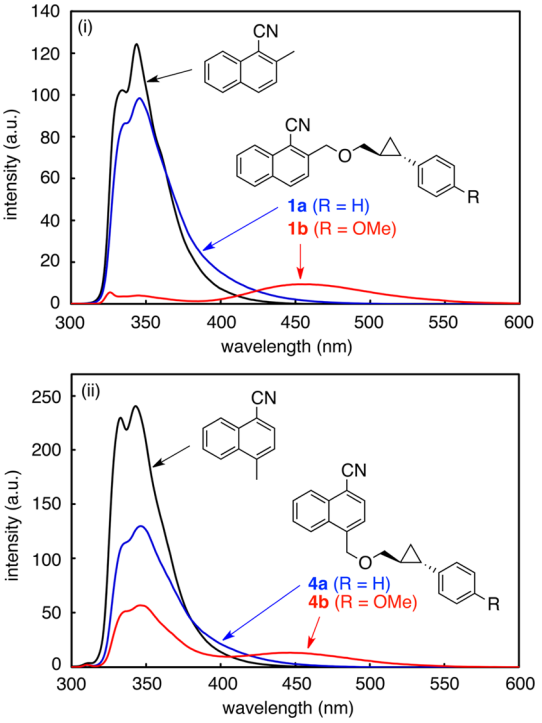

Figure 4. Fluorescence spectra of CH_2Cl_2 solutions of (i) **1a,b** and 1-cyano-2-methylnaphthalene (1×10^{-4} M, λ_{ex} = 326 nm), and (ii) **4a**, 1-cyano-4-methylnaphthalene (1×10^{-4} M, λ_{ex} = 311 nm), and **4b** (5×10^{-5} M, λ_{ex} = 311 nm).

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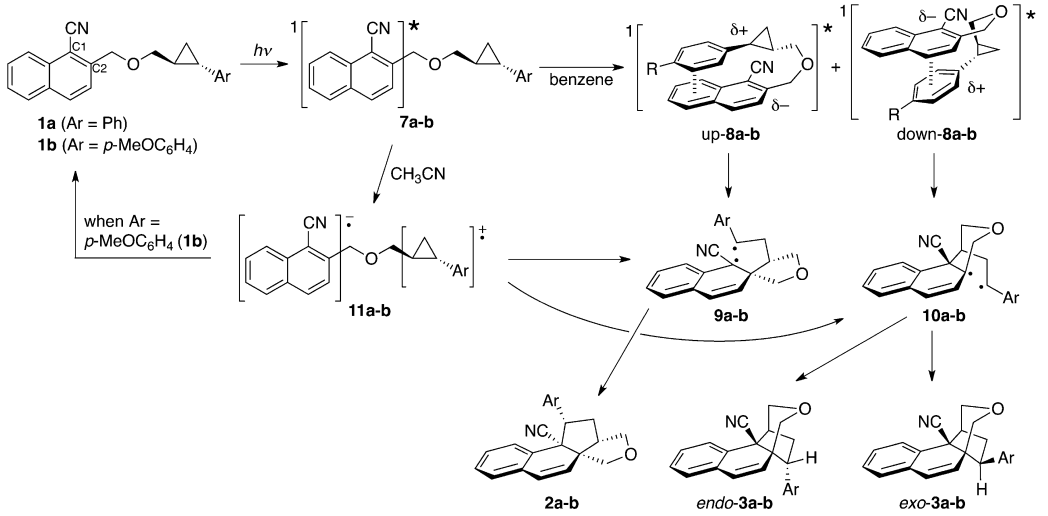
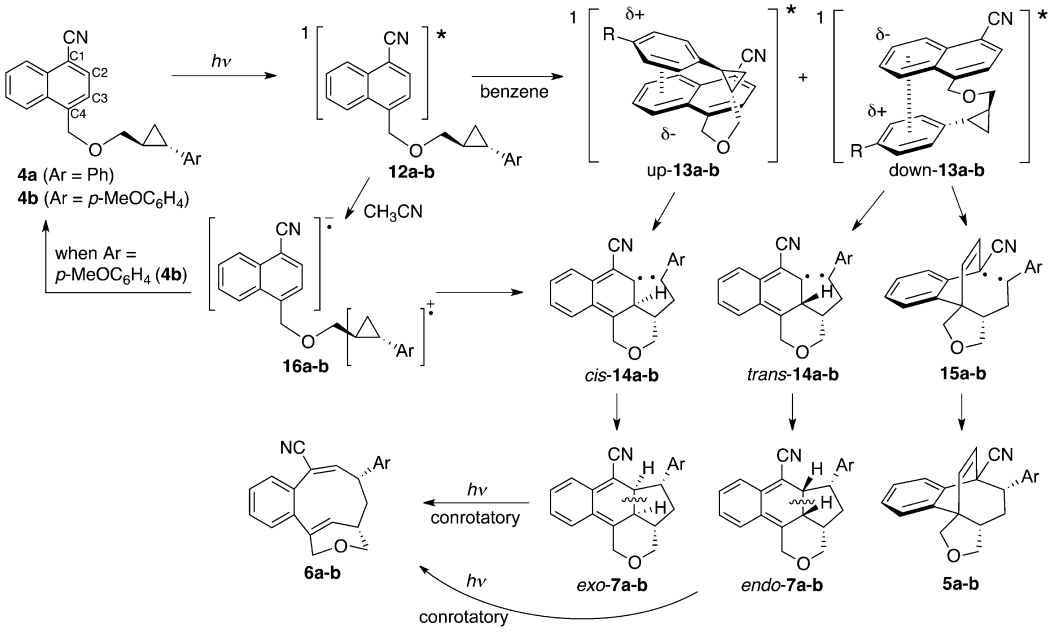
Scheme 4. Possible Mechanistic Pathways for the Intramolecular [3+2] Photocycloaddition Reactions of 1a,b



Scheme 5. Possible Mechanistic Pathways for the Intramolecular Photoreactions of 4a,b



nm). A comparison of the fluorescence spectra of these substances with those of 1-cyano-2-methylnaphthalene and 1-cyano-4-methylnaphthalene showed that emissions from **1a,b** and **4a,b** are partially quenched by the linked phenylcyclopropyl group. On the other hand, the *p*-methoxy analogs **1b** and **4b** not only display monomer emission from localized cyanonaphthalene excited states but also intramolecular exciplex emission at 452 (**1b**) and 447 (**4b**) nm, respectively. Although it is not obvious why **1b** shows stronger intramolecular exciplex emission than **4b**, we would like to suggest that the origin of this difference comes from higher degree of π-π interaction between naphthalene ring and anisyl group in the intramolecular exciplexes formed from **1b** than that from **4b**.

Possible mechanistic pathways for the intramolecular photoaddition reactions of the linked cyclopropane-cyanonaphthalene substrates are outlined in Schemes 4 and 5. It is proposed that cyclopentane ring formation in photoreactions of **1** in benzene (Scheme 4) occurs in a stepwise manner like those of the corresponding intermolecular processes.[6] In the route for these photoreactions, the 1-cyanonaphthalene localized excited state **7** produced by photoirradiation of **1** forms two possible intramolecular singlet exciplexes depicted as up-**8** and down-**8**. Exciplex formation in these cases is likely driven by moderate charge transfer interactions between the phenylcyclopropane donor and excited cyanonaphthalene acceptor moieties. The relative orientations of the interacting arene groups in up-**8** and down-**8** should govern the regiochemistry of C−C bond formation producing biradical intermediates. For example, up-**8** should undergo C−C bond formation at the 2-position of the cyanonaphthalene ring to generate biradical **9** while down-**8** should produce biradical **10** by C−C bonding at the 1-position. Biradical coupling of **9** then forms **2** while that of **10** produces *endo*-**3** and *exo*-**3**. On the other hand, photoreactions of **1a-b** in CH_3CN can also takes place via a pathway initiated by photoinduced electron transfer (PET) from the phenylcyclopropane donor to the excited 1-cyanonaphthalene acceptor to give the zwitterionic biradical **11**. Two regiochemically different modes of nucleophilic addition of the cyanonaph-

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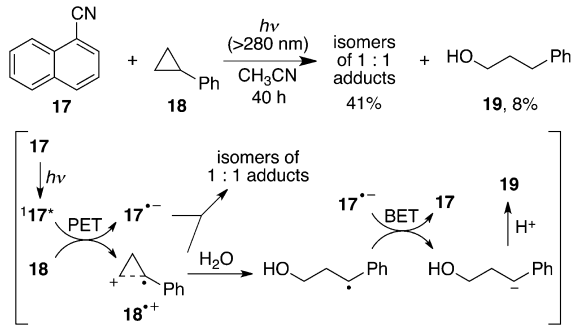
thalene radical anion to the phenylcyclopropane radical cation in **11** would produce biradical intermediates **9** and **10**.

The mechanisms for photoreactions of 4-linked-1-cyanonaphthalenes **4a**,**b** are shown in Scheme 5. The routes followed in these processes take place via the excited state species **12**, and are similar to those operating in photoreactions of the 2-linked analogs. The singlet exciplexes up-**13** and down-**13**, serving as intermediates in these reactions, undergo 2,3-[3+2] and 1,4-[4+3] intramolecular photocycloaddition via biradicals *cis*-**14**, *trans*-**14**, and **15** to give *exo*-**7**, *endo*-**7**, and **5**, respectively. *Exo*-**7** and *endo*-**7** have highly conjugated and reactive ortho-quinodimethane groups, as a result they undergo 10π-electron conrotatory ring opening under the photochemical conditions to yield nine-membered ring containing products **6**. An alternative mechanism for photoreaction of **4a** in acetonitrile involves PET in **12a** to form the zwitterionic biradical **16a**, which undergoes C−C bonding to yield biradicals **14a** and **15a**.

PET mechanistic pathways are known[12,13] to be followed in intermolecular photoreactions of arylcyclopropanes with cyanonaphthalenes in CH_3CN. In order to evaluate the possibility that intramolecular PET proceeds in the corresponding intramolecular reactions described above, ΔG values for single electron transfer (SET) were estimated by using the Rehm−Weller equation, $\Delta G = 23.06(E^{ox}(D/D^+) - E^{red}(A^-/A) - e^2/\varepsilon a) - E_{0-0}$; $e^2/\varepsilon a = 0056$.[14] Based on oxidation potentials of phenylcyclopropane (**18**, $E^{ox}_{1/2}$ = +1.38 V vs Ag/Ag$^+$[13a]) and *p*-methoxyphenylcyclopropane ($E^{ox}_{1/2}$ = +1.02 V vs Ag/Ag$^+$[13a]), the reduction potential of 1-cyanonaphthalene (**17**, $E^{red}_{1/2}$ = −2.22 V vs Ag/Ag$^+$[15]), and excitation energy of **17** (E_{0-0} = 89.4 kcal/mol[12a]), ΔG values for SET from **18** and *p*-methoxyphenylcyclopropane to the excited 1-cyanonaphthalene are calculated to be −6.1 and −14.4 kcal/mol, respectively. These negative ΔG values indicate that PET can occur when mixtures of these substrates are irradiated in CH_3CN solutions.

Furthermore, we explored the intermolecular photoreaction by irradiating a 1:1 mixture of **17** and **18** in CH_3CN for 40 h (Scheme 6). This process produces a mixture of 14 isomeric

Scheme 6. Intermolecular Photoreaction of 1-Cyanonaphthalene with Phenylcyclopropane in CH_3CN



1:1 adducts (m/z = 269, 271, and 273) along with 3-phenylpropanol (**19**) in 41% and 8% respective yields. In contrast, no photoreaction occurs between **17** with **18** (30 h irradiation) when benzene is used as solvent. Formation of **19** in the photoreaction of **17** and **18** in CH_3CN suggests that the cyclopropane radical cation **18**$^{+\cdot}$ is generated as an intermediate in this process. Moreover, the highly nonselective nature of the intermolecular reaction of **17** and **18** is expected based on the fact that many modes exists for reactions of the intermediate radical ions **17**$^{-\cdot}$ and **18**$^{+\cdot}$.

CONCLUSION

In conclusion, intramolecular photoreactions of 2-arylcyclopropane substituted 1-cyanonaphthalenes take place to form intramolecular [3+2] photocycloadducts. The products of these reactions arise by addition of the cyclopropane moiety across the 1,2-positions of the naphthalene ring in a head-to-head and head-to-tail manner. On the other hand, intramolecular photoreactions of the analogous 4-arylcyclopropane substituted 1-cyanonaphthalenes produce both 2,3-[3+2] and 1,4-[4+3] intramolecular photocycloadducts. The results of this effort show that the site-selective and stereoselective nature of these photochemical reactions make them ideally suited to the synthesis of structurally complex polycyclic targets.

EXPERIMENTAL SECTION

General Remarks. 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/benzophenone. CH_2Cl_2 was distilled from CaH_2. *N*-Bromosuccinimide was recrystallized from hot H_2O. CCl_4, hexane, and *N*-methyl-2-pyrrolidone were used as purchased. ^{1}H and ^{13}C NMR spectra were recorded with Me_4Si as an internal standard.

*Preparation of 2-(trans-2-Phenylcyclopropyl)methoxymethyl-1-naphthonitrile (**1a**).* To a stirred mixture of 2-methylnaphthalene (42.6 g, 300 mmol), Fe powder (85 mg, 1.5 mmol), I_2 (73 mg, 0.3 mmol), and CCl_4 (100 mL) was slowly added CCl_4 (50 mL) solution of Br_2 (47.9 g, 300 mmol) at 0 °C, and stirred for 2 h at <10 °C. The dark red solution was washed with H_2O and 10% NaOH aq. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was passed through silica gel to remove inpurities. Distillation under reduced pressure gave 1-bromo-2-methylnaphthalene (55.1 g, 83% yield). Pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.62 (s, 3H), 7.34 (d, J = 8.5 Hz, 1H), 7.43−7.48 (m, 1H), 7.53−7.58 (m, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H) ppm. A mixture of 1-bromo-2-methylnaphthalene (11.8 g, 53.2 mmol), CuCN (11.8 g, 131.6 mmol), and *N*-methyl-2-pyrrolidone (70 mL) was heated to 200 °C by an oil bath and stirred for 30 min. The mixture was cooled to room temperature, 10% NH_3 aq and $CHCl_3$ were added and shaken. The organic layer was concentrated in vacuo. The brown residue was separated by silica gel column chromatography (eluent; hexane:AcOEt = 3:1) to give 1-cyano-2-methylnaphthalene (8.77 g, 52.5 mmol, 99% yield). Colorless needles: mp 81−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.40 (d, J = 8.5 Hz, 1H), 7.55 (m, 1H), 7.66 (m, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H) ppm. A CCl_4 (60 mL) solution of 1-cyano-2-methylnaphthalene (7.77 g, 46.5 mmol), *N*-bromosuccinimide (8.28 g, 46.5 mmol), and benzoyl peroxide (312 mg, 1.3 mmol) was stirred and refluxed for 3 h. The precipitate was removed by filtration, and the filtrate was concentrated in vacuo. The solid (2-bromomethyl-1-cyanonaphthalene, 10.9 g, 44.5 mmol, 96% yield) was used without purification. White solid: mp 80−81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (s, 2H), 7.62 (m, 2H), 7.72 (m, 1H), 7.91 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H) ppm. To a suspension of NaH (60% in mineral oil, 0.780 g, 19.5 mmol) in THF (10 mL) was slowly added cinnamyl alcohol (2.01 g, 15.0 mmol) under argon atmosphere, and stirred under reflux for 30 min. To the solution was added THF (100 mL) solution of 2-bromomethyl-1-cyanonaphthalene (3.69 g, 15.0 mmol) at 0 °C and stirred for 1 h, then stirred at room temperature for 1 h. Brine and Et_2O were added and shaken. The organic layer was separated, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The brown oil was purified by silica gel column chromatography (eluent; hexane:AcOEt = 5:1) to give 1-cyano-2-(*trans*-3-phenyl-2-propenyloxymethyl)naphthalene (2.74 g, 61% yield). Colorless needles: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30

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(dd, J = 6.2, 1.4 Hz, 2H), 4.97 (s, 2H), 6.37 (m, 1H), 6.69 (d, J = 15.8 Hz, 1H), 7.30 (m, 5H), 7.60 (m, 1H), 7.70 (m, 2H), 7.91 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 8.7 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H) ppm; MS (EI+) m/z (relative intensity), 105 (100), 167 (31), 299 (1, M^+). To a solution containing Et_2Zn (1.0 M in hexanes, 14.0 mL, 14.0 mmol) and CH_2Cl_2 (14.0 mL) was added CH_2Cl_2 (7.0 mL) of CF_3COOH (1.08 mL, 14.0 mmol) very slowly at 0 °C under argon atmosphere and stirred for 20 min.[16] To the solution was added CH_2Cl_2 (7.0 mL) solution of CH_2I_2 (1.13 mL, 14.0 mmol), and stirred at 0 °C for 20 min. Then CH_2Cl_2 (7.0 mL) solution of 1-cyano-2-(*trans*-3-phenyl-2-propenyloxymethyl)naphthalene (2.1 g, 7.0 mmol) was added at 0 °C, and stirred at room temperature for 60 min. 0.1 N HCl (35 mL) was added to quench excess Et_2Zn. H_2O and Et_2O were added and shaken. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent; hexane:AcOEt = 5:1) and recycling preparative HPLC (GPC, eluent; $CHCl_3$) to give 2-(*trans*-2-phenylcyclopropyl)methoxymethyl-1-naphthonitrile (**1a**, 1.40 g, 64% yield). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (m, 2H), 1.49 (m, 1H), 1.86 (m, 1H), 3.61 (m, 2H), 4.95 (s, 2H), 7.04−7.16 (m, 3H), 7.20−7.27 (m, 2H), 7.59 (m, 1H), 7.68 (m, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 21.8, 22.7, 70.6, 74.5, 108.3, 116.0, 125.0, 125.0, 125.5, 125.7, 127.1, 128.1, 128.3, 128.5, 132.1, 132.2, 132.8, 142.1, 142.8 ppm; IR (neat) ν 1604, 2218 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 166 (100), 313 (8, M^+). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 84.03; H, 6.09; N, 4.41.

*Preparation of 2-(trans-2-p-Methoxyphenylcyclopropyl)-methoxymethyl-1-naphthonitrile (**1b**).* To a MeOH (70 mL) solution of *trans*-3-(*p*-methoxyphenyl)propenal (4.87 g, 30.0 mmol) was slowly added $NaBH_4$ (1.37 g, 36.0 mmol) at 0 °C, and stirred for 5 min. Ice water was added to quench excess $NaBH_4$. Et_2O was added and shaken. The organic layer was concentrated in vacuo. The solid (*trans*-3-(*p*-methoxyphenyl)-2-propen-1-ol, 4.72 g, 28.8 mmol, 96% yield was used without purification. White powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, J = 6.0 Hz, 1H), 3.81 (s, 3H), 4.30 (m, 2H), 6.19−6.28 (m, 1H), 6.56 (d, J = 15.9 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H) ppm. Reaction of this alcohol with 2-bromomethyl-1-cyanonaphthalene was carried out under similar conditions described in the preparation of **1a** to give 1-cyano-2-[*trans*-3-(*p*-methoxyphenyl)-2-propenyloxymethyl]naphthalene. White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 4.29 (dd, J = 6.3, 1.2 Hz, 2H), 4.95 (s, 2H), 6.22 (m, 1H), 6.63 (d, J = 15.8 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.60 (m, 1H), 7.69 (m, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H) ppm; IR (KBr) ν 2218 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 135 (100), 163 (93), 329 (11, M^+). Simmons-Smith reaction of this alkene was carried out under similar conditions described in the preparation of **1a**. Purification by recrystallization from hexane-EtOH gave pure 2-(*trans*-2-*p*-methoxyphenylcyclopropyl)methoxymethyl-1-naphthonitrile (**1b**). Colorless needles: mp 81−82 °C (EtOH/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (m, 2H), 1.41 (m, 1H), 1.82 (m, 1H), 3.60 (m, 2H), 3.77 (s, 3H), 4.95 (s, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 7.59 (m, 1H), 7.69 (m, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 21.2, 22.3, 55.5, 70.7, 74.8, 108.4, 113.8, 116.2, 125.2, 127.0, 127.2, 127.2, 128.4, 128.6, 132.2, 132.4, 133.0, 134.2, 143.0, 157.6 ppm; IR (KBr) ν 2214 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 147 (100), 166 (50), 343 (8, M^+). Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.41; H, 6.17; N, 4.08.

*Preparation of 4-(trans-2-Phenylcyclopropyl)methoxymethyl-1-naphthonitrile (**4a**).* To a mixture of 1-methylnaphthalene (8.00 g, 56.3 mmol), Fe powder (85 mg, 1.5 mmol), I_2 (73 mg, 0.3 mmol), and CCl_4 (25 mL) was slowly added a CCl_4 (5 mL) solution of Br_2 (9.01 g, 2.91 mL, 56.3 mmol) at 0 °C, and stirred for 2 h. The solution was washed with sat $Na_2S_2O_3$ aq, 10% NaOH aq, and brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The solid (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), and *N*-methyl-2-pyrrolidone (70 mL) was heated to 200 °C by an oil bath, and stirred for 30 min. The mixture was cooled to room temperature, 10% NH_3 aq and $CHCl_3$ were added, and the mixture was shaken. The organic layer was concentrated in vacuo. The brown residue was separated by silica gel column chromatography (eluent; hexane:AcOEt = 3:1) to give 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), 7.37 (d, J = 7.3 Hz, 1H), 7.67 (m, 2H), 7.81 (d, J = 7.3 Hz, 1H), 8.08 (m, 1H), 8.25 (m, 1H) 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), and benzoyl peroxide (312 mg, 1.3 mmol) was stirred and refluxed for 3 h. The precipitate was removed by filtration, and the filtrate was concentrated in vacuo. The solid (4-bromomethyl-1-cyanonaphthalene, 10.9 g, 44.5 mmol, 96% yield) was used without purification. Yellow solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.93 (s, 2H), 7.59 (d, J = 7.3 Hz, 1H), 7.75 (m, 2H), 7.86 (d, J = 7.3 Hz, 1H), 8.23 (m, 1H), 8.31 (m, 1H) ppm. To a suspension of NaH (60% in mineral oil, 0.780 g, 19.5 mmol) in THF (10 mL) was slowly added cinnamyl alcohol (2.01 g, 15.0 mmol) under argon atmosphere. The solution was stirred and refluxed for 30 min. To the solution was added THF (100 mL) solution of 4-bromomethyl-1-cyanonaphthalene (3.69 g, 15.0 mmol) at 0 °C and it was stirred for 1 h, then it was stirred at room temperature for 1 h. Brine and Et_2O was added and shaken. The organic layer was separated, dried over Na_2SO_4, filtrated, and concentrated in vacuo. Product was purified by silica gel column chromatography (eluent; hexane:AcOEt = 5:1) to give 1-cyano-4-(*trans*-3-phenyl-2-propenyloxymethyl)naphthalene (2.74 g, 61% yield). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (dd, J = 6.0, 1.4 Hz, 2H), 5.05 (s, 2H), 6.35 (m, 1H), 6.67 (d, J = 15.9 Hz, 1H), 7.20−7.42 (m, 5H), 7.64 (d, J = 7.1 Hz, 1H), 7.69 (m, 2H), 7.90 (d, J = 7.3 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 69.9, 71.6, 110.4, 117.9, 124.3, 124.5, 125.4, 125.9, 126.5, 127.7, 127.9, 128.3, 128.6, 131.0, 132.2, 132.4, 133.1, 136.4, 140.0 ppm; IR (neat) ν 2222 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 105 (100), 166 (63), 299 (8, M^+). To a solution containing Et_2Zn (1.0 M in hexanes, 14.0 mL, 14.0 mmol) and CH_2Cl_2 (14.0 mL) was added CH_2Cl_2 (7.0 mL) of CF_3COOH (1.08 mL, 14.0 mmol) very slowly at 0 °C under argon atmosphere and stirred for 20 min.[16] To the solution was added CH_2Cl_2 (7.0 mL) solution of CH_2I_2 (1.13 mL, 14.0 mmol), and stirred at 0 °C for 20 min. Then CH_2Cl_2 (7.0 mL) solution of 1-cyano-4-(*trans*-3-phenyl-2-propenyloxymethyl)naphthalene (2.1 g, 7.0 mmol) was added at 0 °C, and it was stirred at room temperature for 60 min. 0.1 N HCl (35 mL) was added to quench excess Et_2Zn. H_2O and Et_2O were added and shaken. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent; hexane:AcOEt = 5:1) and recycling preparative HPLC (GPC, eluent; $CHCl_3$) to give 4-(*trans*-2-phenylcyclopropyl)methoxymethyl-1-naphthonitrile (**4a**, 1.40 g, 64% yield). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (m, 2H), 1.48 (m, 1H), 1.83 (m, 1H), 3.60 (d, J = 6.6 Hz, 2H), 5.01 (s, 2H), 7.01−7.06 (m, 2H), 7.10−7.17 (m, 1H), 7.20−7.27 (m, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.60 (m, 1H), 7.67 (m, 1H), 7.83 (d, J = 7.3 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.0, 22.8, 70.3, 74.4, 110.2, 117.8, 124.3, 124.4, 125.6, 125.7, 125.7, 127.6, 128.2, 128.2, 130.9, 132.1, 132.3, 140.1, 142.1 ppm; IR (neat) ν 2222 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 117 (89), 166 (100), 313 (11, M^+); HRMS (EI+) Calcd for $C_{22}H_{19}NO$: 313.1467, Found: 313.1459.

*Preparation of 4-(trans-2-p-Methoxyphenylcyclopropyl)-methoxymethyl-1-naphthonitrile (**4b**).* Reaction of 4-bromomethyl-1-cyanonaphthalene (described in preparation of **4a**) with *trans*-3-(*p*-methoxyphenyl)-2-propen-1-ol (described in preparation of **1b**) was carried out under similar conditions described in preparation of **4a** to give 1-cyano-4-[*trans*-3-(*p*-methoxyphenyl)-2-propenyloxymethyl]-naphthalene. White solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.27 (dd, J = 6.3, 1.2 Hz, 2H), 5.00 (s, 2H), 6.20 (m, 1H), 6.59

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(d, J = 15.9 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 7.53−7.70 (m, 3H), 7.84 (d, J = 7.3 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 7.5 Hz, 1H) ppm; MS (EI+) m/z (relative intensity) 135 (100), 166 (31), 329 (16, M^+). Simmons−Smith reaction of this alkene was carried out under similar conditions described in the preparation of **4a**. Purification by recrystallization from hexane-EtOH gave pure 4-(*trans*-2-*p*-methoxyphenylcyclopropyl)methoxymethyl-1-naphthonitrile (**4b**). Colorless needles: mp 197−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (m, 2H), 1.40 (m, 1H), 1.78 (m, 1H), 3.58 (d, J = 6.7 Hz, 2H), 3.75 (s, 3H), 5.00 (s, 2H), 6.78 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 7.4 Hz, 1H), 7.57−7.68 (m, 2H), 7.82 (d, J = 7.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 21.2, 22.2, 55.4, 70.3, 74.5, 110.1, 113.8, 117.8, 124.3, 124.3, 125.7, 126.8, 127.5, 128.2, 130.8, 132.0, 132.2, 134.1, 140.1, 157.6 ppm; IR (KBr) ν 2222 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 147 (100), 166 (36), 343 (12, M^+); HRMS (EI+) Calcd for $C_{23}H_{21}NO_2$: 343.1572, Found: 343.1575.

Photoreaction. A benzene, CH_2Cl_2 or CH_3CN solution (10 mL), containing **1** or **4** (10 mM), in cylindrical Pyrex vessels (ϕ = 8 mm) was purged with argon for 15 min and then the vessel was sealed. The solution was irradiated by using a 300 W high pressure mercury lamp at room temperature (>280 nm light). The temperature of the solution during irradiation was maintained around room temperature by using circulated cooling water.

(1S,2aS*,5aS*,11bS*)-11b-Cyano-1-phenyl-1,2,2a,3,5,11b-hexahydrobenzo[4,5]indeno[1,7a-c]furan (**2a**).* Colorless blocks: mp 188−191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (m, 2H), 2.90 (m, 1H), 3.24 (m, 1H), 3.42 (d, J = 10.4 Hz, 1H), 3.96 (m, 1H), 4.05 (m, 1H), 4.31 (d, J = 10.3 Hz, 1H), 5.71 (d, J = 9.8 Hz, 1H), 6.45 (d, J = 9.8 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 6.89−7.01 (m, 3H), 7.14 (m, 1H), 7.18−7.31 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.9, 52.6, 57.5, 58.1, 60.4, 74.1, 75.5, 119.4, 124.1, 127.2, 127.3, 127.8, 127.9, 128.5, 129.1, 129.2, 129.2, 129.4, 130.8, 135.2 ppm; IR (KBr) ν 2234 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 117 (66), 179 (100), 313 (46, M^+). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 84.08; H, 6.14; N, 4.41.

(1S,4aR*,10bR*,11R*)-10b-Cyano-11-phenyl-1,2,4,10b-tetrahydro-4a,1-ethanobenzo[f]isochromene (endo-**3a**).* Colorless blocks: mp 203−204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (m, 2H), 3.17 (m, 1H), 3.72 (m, 1H), 3.82 (d, J = 11.3 Hz, 1H), 4.03 (dd, J = 11.6, 2.7 Hz, 1H), 4.25 (d, J = 11.3 Hz, 1H), 4.34 (d, J = 11.7 Hz, 1H), 5.35 (d, J = 9.6 Hz, 1H), 6.18 (d, J = 9.6 Hz, 1H), 6.23 (d, J = 7.3 Hz, 2H), 6.79 (d, J = 7.4 Hz, 1H), 6.87 (m, 2H), 6.97 (m, 1H), 7.27 (m, 1H), 7.34−7.46 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.0, 42.6, 49.5, 51.5, 51.7, 70.7, 75.5, 120.0, 123.4, 126.1, 126.6, 127.1, 127.9, 128.6, 128.9, 129.1, 129.2, 129.9, 134.9, 140.5 ppm; IR (KBr) ν 2224 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 91 (89), 146 (100), 313 (2, M^+); HRMS (EI+) Calcd for $C_{22}H_{19}NO$: 313.1467, Found: 313.1468.

(1S,4aR*,10bR*,11R*)-10b-Cyano-11-p-methoxyphenyl-1,2,4,10b-tetrahydro-4a,1-ethanobenzo[f]isochromene (endo-**3b**).* Colorless solid: mp 146−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (m, 1H), 2.35 (m, 1H), 3.15 (m, 1H), 3.67 (m, 1H), 3.68 (s, 3H), 3.80 (d, J = 11.3 Hz, 1H), 4.02 (dd, J = 11.5, 2.6 Hz, 1H), 4.24 (d, J = 11.3 Hz, 1H), 4.32 (d, J = 11.7 Hz, 1H), 5.34 (d, J = 9.6 Hz, 1H), 6.13 (d, J = 8.8 Hz, 2H), 6.22 (d, J = 9.6 Hz, 1H), 6.42 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 7.2 Hz, 1H), 7.28 (m, 1H), 7.34−7.45 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.5, 42.5, 49.4, 50.8, 51.6, 55.3, 70.7, 75.4, 112.6, 120.0, 123.4, 126.7, 127.9, 128.8, 129.0, 129.2, 129.5, 129.9, 132.6, 134.9, 157.7 ppm; IR (KBr) ν 2228 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 135 (56), 147 (100), 343 (10, M^+); HRMS (EI+) Calcd for $C_{23}H_{21}NO_2$: 343.1572, Found: 343.1578.

(1S,4aR*,10bR*,11S*)-10b-Cyano-11-phenyl-1,2,4,10b-tetrahydro-4a,1-ethanobenzo[f]isochromene (exo-**3a**).* Colorless blocks: mp 150−153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (m, 1H), 2.34 (m, 1H), 3.10 (m, 2H), 3.49 (d, J = 11.8 Hz, 1H), 3.96 (d, J = 11.9 Hz, 1H), 4.08 (dd, J = 11.5, 2.9 Hz, 1H), 4.37 (d, J = 11.5 Hz, 1H), 5.49 (d, J = 9.8 Hz, 1H), 6.70 (d, J = 9.6 Hz, 1H), 7.19−7.32 (m, 4H), 7.32−7.48 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.1, 41.7, 49.0, 50.7, 51.4, 68.9, 71.2, 119.5, 123.9, 126.9, 128.0, 128.1, 128.1, 128.3, 129.0, 129.1, 129.1, 130.5, 132.4, 138.4 ppm; IR (KBr) ν 2227 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 91 (100), 145 (87), 313 (1, M^+). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 84.27; H, 6.07; N, 4.51.

(1S,4aR*,10bR*,11S*)-10b-Cyano-11-p-methoxyphenyl-1,2,4,10b-tetrahydro-4a,1-ethanobenzo[f]isochromene (exo-**3b**).* Colorless solid: mp 125−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (m, 2H), 3.06 (m, 2H), 3.51 (d, J = 11.8 Hz, 1H), 3.78 (s, 3H), 3.96 (d, J = 11.9 Hz, 1H), 4.07 (dd, J = 11.5, 2.8 Hz, 1H), 4.37 (d, J = 11.3 Hz, 1H), 5.48 (d, J = 9.5 Hz, 1H), 6.69 (d, J = 9.6 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.26−7.46 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 41.6, 48.3, 50.6, 51.3, 55.4, 68.9, 71.2, 113.5, 119.5, 123.9, 127.9, 128.3, 129.0, 129.0, 130.0, 130.4, 130.6, 130.6, 132.4, 158.4 ppm; IR (KBr) ν 2226 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 135 (66), 147 (100), 343 (8, M^+); HRMS (EI+) Calcd for $C_{23}H_{21}NO_2$: 343.1572, Found: 343.1565.

(3aS,5S*,6R*,10bS*)-6-Cyano-5-phenyl-1,3,3a,4,5,6-hexahydro-6,10b-ethenobenzo[3,4]cyclohepta[1,2-c]furan (**5a**).* Colorless blocks: mp 226−227 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (m, 1H), 1.87 (m, 1H), 2.46 (m, 1H), 3.13−3.24 (m, 2H), 4.01 (m, 1H), 4.03 (d, J = 9.6 Hz, 1H), 4.67 (d, J = 9.3 Hz, 1H), 6.40 (d, J = 8.5 Hz, 1H), 6.67 (d, J = 8.5 Hz, 1H), 6.98 (m, 2H), 7.26−7.34 (m, 3H), 7.38−7.56 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.5, 42.9, 45.5, 49.4, 50.6, 73.5, 75.2, 120.4, 124.0, 126.0, 126.8, 127.9, 128.1, 128.6, 128.8, 133.5, 135.2, 136.7, 138.1, 141.9 ppm; IR (KBr) ν 2240 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 91 (100), 117 (81), 313 (12, M^+); HRMS (EI+) Calcd for $C_{22}H_{19}NO$: 313.1467, Found: 313.1470.

(3aS,5S*,6R*,10bS*)-6-Cyano-5-p-methoxyphenyl-1,3,3a,4,5,6-hexahydro-6,10b-ethenobenzo[3,4]cyclohepta[1,2-c]furan (**5b**).* White solid: mp 181−183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (m, 1H), 1.84 (m, 1H), 2.45 (m, 1H), 3.12−3.20 (m, 2H), 3.79 (s, 3H), 4.01 (m, 2H), 4.66 (d, J = 9.3 Hz, 1H), 6.39 (d, J = 8.7 Hz, 1H), 6.66 (d, J = 8.5 Hz, 1H), 6.82 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 7.38−7.53 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 43.1, 44.6, 49.8, 50.6, 55.4, 73.5, 75.2, 113.9, 120.5, 123.9, 125.9, 126.8, 128.1, 129.0, 133.5, 134.1, 135.1, 136.6, 138.0, 159.0 ppm; IR (KBr) ν 2244 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 134 (74), 147 (100), 343 (18, M^+); HRMS (EI+) Calcd for $C_{23}H_{21}NO_2$: 343.1572, Found: 343.1568.

*trans-(1(12)Z,8E)-9-Cyano-7-phenyl-4,5,6,7-tetrahydro-2H-1,5-(metheno)benzo[d][1]oxacycloundecin (**6a**).* Colorless blocks: mp 147−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (m, 1H), 2.33 (m, 1H), 2.81 (m, 1H), 3.58 (m, 1H), 3.74 (m, 1H), 4.10−4.19 (m, 2H), 4.34 (m, 1H), 5.87 (m, 1H), 6.69 (d, J = 11.4 Hz, 1H), 7.10 (m, 2H), 7.20−7.34 (m, 4H), 7.34−7.40 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.1, 41.3, 45.9, 68.9, 70.3, 110.8, 120.5, 125.8, 127.3, 127.4, 127.9, 129.0, 129.4, 129.5, 132.9, 133.4, 138.0, 139.7, 141.8, 154.0 ppm; IR (KBr) ν 2212 (CN) cm^{-1}; MS (EI+) m/z (relative intensity) 91 (100), 146 (98), 179 (97), 313 (45, M^+). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.32; H, 6.11; N, 4.47. Found: C, 83.94; H, 6.14; N, 4.43.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01721.

CIF files for **2a**, *endo*-**3a**, *exo*-**3a**, **5a**, and **6a** (ZIP)

NMR spectra for compounds: **1a**,**b**; **2a**; *endo*-**3a**,**b**; *exo*-**3a**,**b**; **4a**,**b**; **5a**,**b**; and **6a**, description of X-ray crystallographic analysis including full-page size ORTEP plots (PDF)

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Notes

The authors declare no competing financial interest.

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