# Photoinduced Electron Transfer Reaction of Mono- and Dicyanonaphthalenes with Allyltrimethylsilane: Synthesis of Benzotricyclo[4.2.1.0³·⁸]nonenes by Reductive Photoallylation and Intramolecular (2π+2π) Photocycloaddition

**Toshinori Nishiyama, Kazuhiko Mizuno,\* Yoshio Otsuji, and Hiroo Inoue**

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593, Japan

*Abstract:* Irradiation of an acetonitrile-methanol (4:1) solution containing 1-cyanonaphthalene and allyltrimethylsilane (1) through Pyrex filter (>280 nm) regioselectively gave 3-cyano-4,5-benzotricyclo[4.2.1.0³·⁸]-4-nonene. The photoreaction of 2-cyanonaphthalene, 1-cyano-2-methylnaphthalene, 1-cyano-4-methylnaphthalene, 1,5- and 2,3-dicyanonaphthalenes with 1 gave the corresponding benzotricyclic compounds also in a regioselective manner. However, the photoreaction of 2,3-disubstituted 1,4-dicyanonaphthalenes with 1 gave no benzotricyclic compounds, but only the allyl substitution and reductive allylation products. These photoreactions were initiated by photoinduced electron transfer from 1 to the excited singlet states of mono- and dicyanonaphthalenes. The reductive allylation products from the former cyanonaphthalenes afforded the benzotricyclic compounds by an intramolecular (2π+2π) photocycloaddition in good yields. The regioselectivity in the allylation reaction is discussed on the basis of the results of MO calculations of the radical anions of mono- and dicyanonaphthalenes.

## INTRODUCTION

Inter- and intramolecular photocycloaddition is a useful tool for the construction of polycyclic compounds.[1] Previously, Mariano et al. reported the photoallylation of iminium salts by allylic silanes.[2] We and others also reported the photoallylation of electron-deficient aromatic compounds, alkenes, and ketones by use of allylic silanes.[3-7]
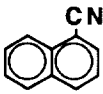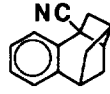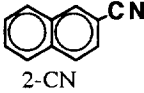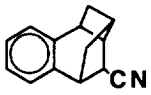


1,4-DCN      **1**         **2**         **3**
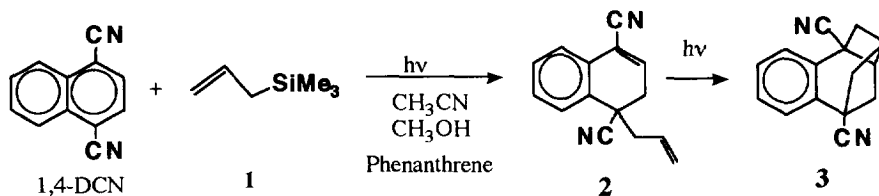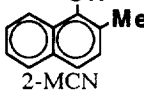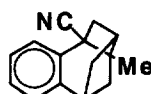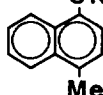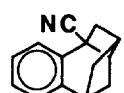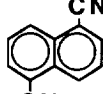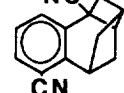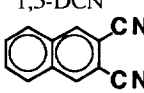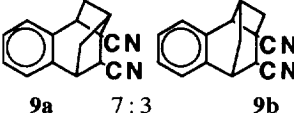
In the course of our studies on the photoreaction of 1,4-dicyanonaphthalene (1,4-DCN) with allyltrimethylsilane (1), we found that benzotricyclic compound (3) was formed under certain conditions.[6] In this photoreaction, the allyl group of 1 first added to 1,4-DCN to give the reductive addition product 2 which was then converted into the tricyclic compound 3 via an intramolecular (2π+2π) photocycloaddition. We have extended this photoreaction to other cyanonaphthalene derivatives to gain insight into the mechanistic features and

synthetic application of the photoreaction. This paper describes the results so far obtained. The regioselectivity in the photoallylation of cyanonaphthalenes is discussed on the basis of the results of MO calculations.

## RESULTS AND DISCUSSION

*Photoreaction of Mono- and Dicyanonaphthalenes with 1.* Irradiation of an acetonitrile-methanol (4:1) solution containing 1-cyanonaphthalene (1-CN, 2 mmol) and **1** (10 mmol) through Pyrex filter (>280 nm) under argon atmosphere gave 3-cyano-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene (**4**) in a 28% yield.[5e] Similarly, irradiation of 2-cyanonaphthalene (2-CN), 1-cyano-2-methylnaphthalene (2-MCN), 1-cyano-4-methyl-naphthalene (4-MCN), and 1,5-dicyanonaphthalene (1,5-DCN), with **1** afforded the benzotricyclic compounds **5, 6, 7**, and **8**. In the case of 2,3-dicyanonaphthalene (2,3-DCN), an isomeric mixture of the benzotricyclic compounds **9a, b** and a small amount of 2-allyl-3-cyanonaphthalene (**9c**) (<1 % yield) were obtained. In the cases of 1-CN, 1,5-DCN, and 2,3-DCN, the addition of phenanthrene (Phen) to the reaction system was effective to obtain the tricyclic compounds **4, 8**, and **9a-b**.[6] However, the formation of **5, 6**, and **7** was suppressed by the addition of Phen. The results are summarized in Table 1.
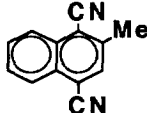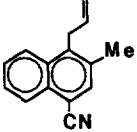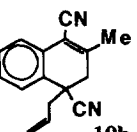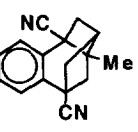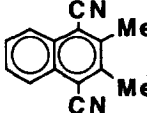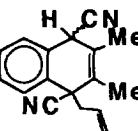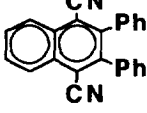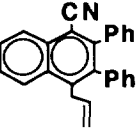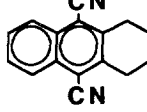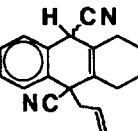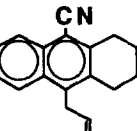
Table 1. Formation of Tricyclic Compounds in the Photoreactions of Mono- and Dicyanonaphthalenes with Allyltrimethylsilane

| Cyanonaphthalene | Additive | Irradiation time / h | Product(s) | Yield / %[a] | |
|---|---|---|---|---|---|
| 1-CN | none | 12 | **4** | 28 | |
| | Phen | 18 | | 40 | |
| 2-CN | none | 96 | **5** | 11 | |
| | Phen | 96 | | 2 | |
| 2-MCN | none | 12 (40)[b] | **6** | 54 | (48)[b] |
| | Phen | 18 | | 15 | |
| 4-MCN | none | 18 (50)[b] | **7** | 20 | (18)[b] |
| | Phen | 18 | | 5 | |
| 1,5-DCN | none | 2 (12)[b] | **8** | 25 | (16)[b] |
| | Phen | 2 | | 38 | |
| 2,3-DCN | none | 2 (3)[b] | **9a** 7:3 **9b** | 69 | (78)[b] |
| | Phen | 2 | **9a, b** (7:3) | 62 | |

[a] GLC yields based on cyanonaphthalenes used. [b] Isolated yields.

The products were isolated by column chromatography on silica gel. Their structures were determined by the spectral properties and elemental analyses.[4b] The ¹H and ¹³C NMR, 2D H-H and H-C COSY spectra of new products were compared with those of 3 whose structure had been confirmed by X-ray crystallography.[6b]

Table 2. Photoreactions of Substituted 1,4-Dicyanonaphthalenes with Allyltrimethylsilane

| Cyanonaphthalene | Additive | Irradiation time / h | Product(s) | | | Yield(s) / %[a] |
|---|---|---|---|---|---|---|
| 2-MDCN | Phen | 1 | 10a 17 % | 10b, c (1:1) 47 %[c] | | 10d 13 % |
| | none | 1 | 10a < 3 %[b] | 10b, c (1.4:1) 90 %[b,c] | | 10d < 3 %[b] |
| DMDCN | Phen | 1.5 | 11 71 %[b,c] | | | |
| | none | 1 | 90 %[b,c] | | | |
| DPDCN | Phen | 1.5 | 13 52 % | | | |
| | none | 1 | 60 %[b] | | | |
| CyDCN | Phen | 1.5 | 14 80 %[b,c] | | | |
| | none | 1 | 14 31%[b,c] | | 16 62 %[b] | |

[a] Isolated yields based on cyanonaphthalenes used. [b] GLC yields. [c] Yields were determined as a mixture of two isomers.

*Photoreaction of 2-Substituted and 2,3-Disubstituted 1,4-Dicyanonaphthalenes with 1.* Irradiation of 1,4-dicyano-2-methylnaphthalene (2-MDCN) with an excess of 1 in acetonitrile-methanol (4:1) gave 10a-d. The product ratio changed by the addition of Phen to the reaction system. Prolonged irradiation resulted in a decrease in the amount of 10b and an increase in the amount of 10d. The photoreaction of 1,4-dicyano-2,3-dimethylnaphthalene (DMDCN) and 9,10-dicyano-1,2,3,4-tetrahydroanthracene (CyDCN) with 1 did not give benzotricyclic compounds, but the reductive addition products, 11 and 14, respectively. The column

chromatography of **11** on silica gel gave **12**. The photoreaction of the sterically hindered 1,4-dicyano-2,3-diphenylnaphthalene (DPDCN) gave only the substitution product **13**. The results are summarized in Table 2.



Irradiation of the reductive allylation products **10c, 12,** and **14** did not give benzotricyclic compounds, and prolonged irradiation of these compounds gave complex mixtures.    Treatment of **11, 12,** and **14** with sodium methoxide in acetonitrile afforded the substitution product **15** and **16** by dehydrocyanation.
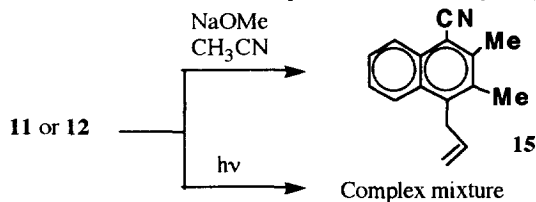


*Stereoselective Deuterium Incorporation.*    Irradiation of an acetonitrile-methanol-O-d$_1$ (6 : 1) solution containing 1-CN and **1** under similar conditions gave the monodeuterated benzotricyclic compound **4-d$_1$** in a highly stereoselective manner.    The photoreaction of 2-CN and 2,3-DCN gave **5-d$_1$** and **9a-d$_1$**, **9b-d$_1$**, respectively.    The structures of the deuterium incorporated products were determined by the analysis of the chemical shifts and coupling constants in their $^1$H NMR spectra.[4b, 6]   We have rationalized that our assigned structures were favorable from our proposed mechanism for the formation of reductive allylation products (See Mechanism and Fig. 1).
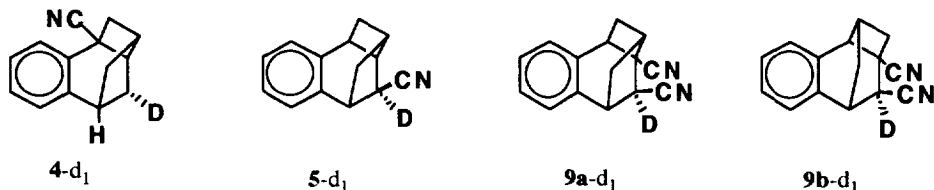


*Fluorescence Quenching and Free Energy Changes.*    Fluorescence of mono- and dicyanonaphthalenes except 2-CN in acetonitrile was efficiently quenched by **1** in nearly diffusion controlled rates.    Exciplex emission was not observed in this solvent.    UV-visible spectra of solutions containing **1** and cyanonaphthalenes did not exhibt any indication of charge transfer interaction between these compounds.    Fluorescence of 2-CN was slightly quenched by **1** and the rate of the fluorescence quenching was $2.8 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.    Free energy changes ($\Delta G$) for one-electron transfer process from **1** to excited singlet states of cyanonaphthalenes were calculated to be negative except 2-CN by use of the Rehm-Weller equation.[8]

Table 3. Rate Constants for Fluorescence Quenching of Mono- and Dicyanonaphthalenes
by Allyltrimethylsilane (1) and Calculated $\Delta G$ Values for One-Electron Transfer Process from
1 to Excited Singlet States of Cyanonaphthalenes in Acetonitrile

| Compd | $E_{1/2}^{red}$ / V [a] | Life time $\tau$ / ns | $kq\tau$ / mol$^{-1}$dm$^3$ | $kq \times 10^{-9}$ / mol$^{-1}$dm$^3$s$^{-1}$ | $\Delta G$ / kJ mol$^{-1}$ [b] |
|---|---|---|---|---|---|
| 1-CN | -2.22 | 6.8 | 46.6 | 6.9 | -0.58 |
| 2-CN | -2.35 | 10.6 | 3.0 | 0.28 | 14.9 |
| 2-MCN | -2.31 | 10.9 | 27.8 | 2.6 | -4.44 |
| 4-MCN | -2.31 | 8.2 | 31.5 | 3.8 | -1.54 |
| 1,5-DCN | -1.80 | 8.5 | 64.6 | 7.6 | -12.2 |
| 2,3-DCN | -1.85 | 13.2 | 23.4 | 1.8 | -19.9 |
| 2-MDCN | -1.64 | 7.3 | 62.8 | 8.6 | -27.6 |
| DMDCN | -1.70 | 7.0 | 53.2 | 7.6 | -21.8 |
| DPDCN | -1.55 | 9.1 | 27.9 | 3.1 | -36.3 |
| CyDCN | -1.67 | 7.4 | 13.9 | 1.9 | -24.7 |

[a] $E_{p/2}^{red}$ / V vs Ag/AgCl in CH$_3$CN. [b] The oxidation potential of 1 ($E_{p/2}^{ox}$=1.59 V) was used.[6b]

*Mechanism.* The proposed mechanism for the formation of benzotricyclic compounds is shown in Scheme 1, which is similar to that in a previous paper.[6b] The photoreaction is initiated by one-electron transfer from 1 to the excited singlet states of cyanonaphthalenes A to give free radical ions 1$^{+•}$ and A$^{-•}$ via the radical ion pair. This process is likely to be exothermic from the fluorescence quenching experiments and the free energy change calculation. The allyl radical, which is produced by the cleavage of the C-Si bond of 1$^{+•}$,[4] adds to A$^{-•}$ in a regioselective manner to give the anionic intermediate ACN$^-$. Its protonation gives the reductive allylation product (ACNH). It is notably here that the protonation occurs stereoselectively from the less hindered site, to give ACNH (Fig. 1). The regioselective allylation of mono- and dicyanonaphthalene is reasonably explained from the spin density of A$^{-•}$ (Table 4).[9]

Scheme 1.

$$^1A^* \ + \ \overset{}{\underset{1}{=\!\!\!\diagdown\!\!-SiMe_3}} \ \overset{h\nu}{\longrightarrow} \ \left[ A^{-•} \cdots\cdots 1^{+•} \right] \longrightarrow A^{-•} \ + \ 1^{+•}$$

$$1^{+•} \ \xrightarrow[-NuSiMe_3^+]{Nu} \ \xrightarrow{A^{-•}} \ [ACN^-] \ \xrightarrow{H^+ (D^+)} \ ACNH(D)$$

S $\xrightarrow{h\nu}$ $^1$S$^*$ $\longrightarrow$ $^3$S$^*$ $\xrightarrow{ACNH}$

$\longrightarrow$ $^3$ACNH$^*$

ACNH $\xrightarrow{h\nu}$ $^1$ACNH$^*$

$^3$ACNH$^*$ $\longrightarrow$ Tricyclic compound(s)

$^3$ACNH$^*$ + Q $\longrightarrow$ ACNH + $^3$Q$^*$ $\longrightarrow$ ACNH + Q

A; Cyanonaphthalene

S; Triplet sensitizer

Nu; Nucleophile

Q; Triplet quencher

ACNH; Reductive allylation product
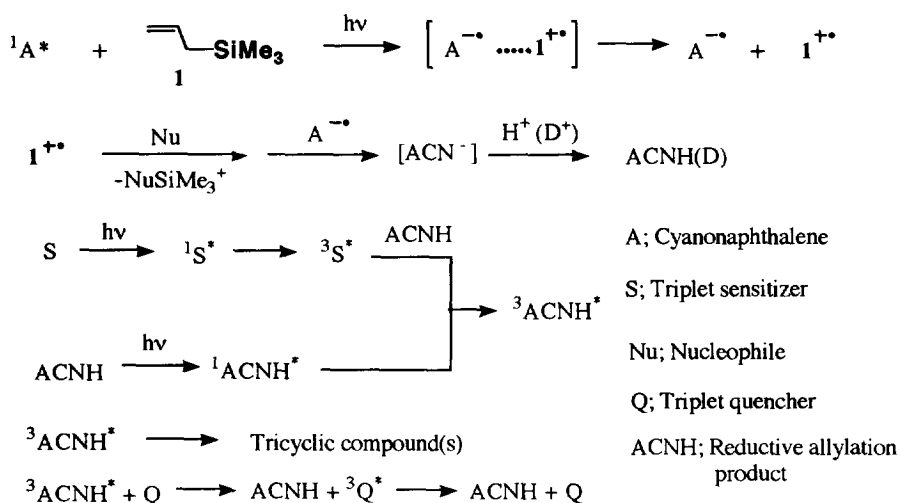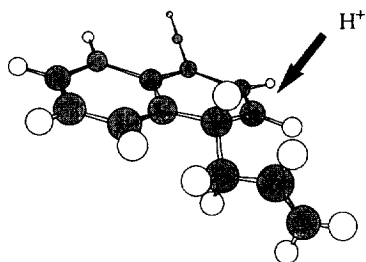
Fig. 1 Hypothetical view for the protonation of allylated anion of 1-CN

The decyanation from ACN⁻ gives the substitution products. In the presence of methanol, the protonation of ACN⁻ occurs in much faster rate than the decyanation. The photoreaction of DMDCN and CyDCN with **1** gave no tricyclic compound, but 1,4-dihydro allylated products. In these photoreactions, the protonation occurred at the less-hindered 4-position. Deuterium incorporation experiment clearly shows that the protonation on A⁻• is unlikely.

Table 4. Calculated Spin Densities and Charge Densities of Radical Anion of Cyanonaphthalenes by UHF-PM3 Molecular Orbital Calculations

| Cyanonaphthalene | Position | Charge | Spin Density |
|---|---|---|---|
| | 1 | -0.1637 | 0.4098 |
| | 2 | -0.1061 | 0.0172 |
| | 3 | 0.0000 | -0.1069 |
| | 4 | -0.2438 | 0.1570 |
| | 5 | -0.1419 | 0.1160 |
| | 6 | -0.1418 | 0.0076 |
| | 1 | -0.2487 | 0.5343 |
| | 2 | -0.0104 | -0.0898 |
| | 1 | -0.2365 | 0.2708 |
| | 2 | -0.0895 | 0.2410 |
| | 3 | -0.1576 | -0.2238 |
| | 4 | -0.2307 | 0.5822 |
| | 1 | -0.2305 | 0.2427 |
| | 2 | -0.0782 | 0.2793 |
| | 3 | -0.1364 | -0.2588 |
| | 4 | -0.2306 | 0.5848 |
| | 1 | -0.1813 | 0.4231 |
| | 2 | -0.2016 | 0.2227 |
| | 3 | 0.0120 | -0.1629 |
| | 4 | -0.2742 | 0.2597 |
| | 1 | -0.2411 | 0.2694 |
| | 2 | -0.0819 | 0.2311 |
| | 3 | -0.1571 | -0.2195 |
| | 4 | -0.2087 | 0.5853 |

The next step is an intramolecular ($2\pi+2\pi$) photocycloaddition of ACNH to give a tricyclic compound. Albini et al. proposed the triplet mechanism for the intramolecular photocycloaddition of **2**.[5d] We also observed that the photocycloaddition of **2** was sensitized by Michler's ketone ($E_T = 255$ kJ mol$^{-1}$) and benzophenone ($E_T = 289$ kJ mol$^{-1}$), and completely quenched by 2-methyl-1,3-butadiene ($E_T = 251$ kJ mol$^{-1}$). Quantum yields ($\Phi$) for the formation of **3** from **2** were measured. In benzophenone-sensitized photocycloaddition, $\Phi$ was 0.3 and much larger than that in the direct photoreaction ($\Phi = 0.025$). The triplet mechanism was also supported by the fact that the formation of **3** was quenched by the addition of pyrene ($E_T = 203$ kJ mol$^{-1}$). The role of pyrene in this photoreaction may be the internal filter, which we have proposed in the previous paper.[6b] Because, the molar absorption coefficient of pyrene at 300-320 nm is more than ca. 100 times that of **2**. In contrast, phenanthrene was effective to produce the tricyclic compounds. Phenanthrene not only acts as a triplet sensitizer ($E_T = 259$ kJ mol$^{-1}$) for the intramolecular ($2\pi+2\pi$) photocycloaddition, but also as a cosensitizer, which was effective to suppress the back-electron transfer from 1,4-DCN$^-$ to **1**$^+$.[6b] From these results the triplet energy of **2** is estimated about 250 kJ mol$^{-1}$.

It is supposed that the intramolecular ($2\pi+2\pi$) photocycloaddition of **10c**, **12** is inhibited by steric hindrance due to cis-methyl groups at the vicinal position. In the case of 2,3-DCN, two isomeric benzotricyclic compounds were produced. This is explained by the Frontier MO theory (Fig. 2).[11] In the ($2\pi+2\pi$) photocycloaddition, HOMO (SOMO)-HOMO and LUMO (SOMO)-LUMO interactions are important. In the case of **2**, steric demand agrees with the requirement from the Frontier MO interaction to give **3**. However, in the case of 2,3-DCN, the sterically favorable **9a** and the compound **9b** predicted from the Frontier MO interaction are formed competitively.



SOMO-HOMO    SOMO-LUMO      SOMO-HOMO    SOMO-LUMO

1-Allyl-1,4-dicyano-1,2-dihydronaphthalene    1-Allyl-2,3-dicyano-1,2-dihydronaphthalene
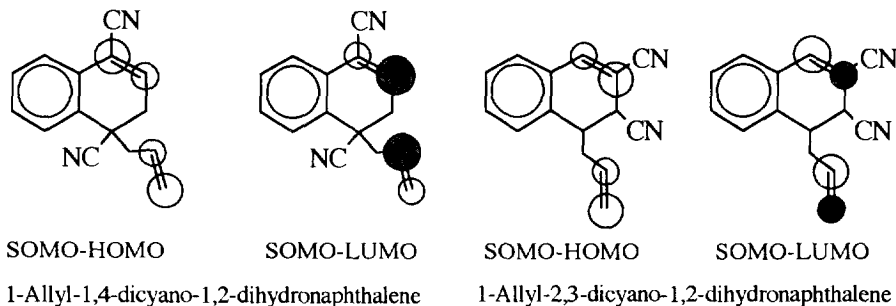
Fig. 2 Molecular orbitals of allylated dicyanodihydronaphthalenes

## EXPERIMENTAL

*Materials.* Acetonitrile was distilled three times over P$_2$O$_5$ and then once over anhydrous CaH$_2$ before use. Mono- and dicyanonaphthalenes were prepared by the method described in the literature.[1] Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.

*General.* Melting points were taken on a hot stage and are uncorrected. $^1$H NMR spectra were recorded on a JEOL JNM-PMX60SI (60 MHz) spectrometer and a JEOL JNM-GX270 (270 MHz) spectrometer for CDCl$_3$ solutions containing tetramethylsilane as an internal standard. $^{13}$C NMR spectra were recorded on a JEOL JNM-GX270 spectrometer for CDCl$_3$ solutions with chloroform ($\delta$=77.05) as an internal standard. Infrared spectra

were obtained on a JASCO FT/IR-5000 spectrophotometer, mass spectra on a Hitachi RMU-6E spectrometer, fluorescence spectra on a JASCO FP-500 spectrofluorometer, and UV-Vis spectra on a JASCO UVIDEC-670.

Elemental analyses were carried out on a YANACO MT-3 elemental analyzer. GLC analyses were performed with a Hitachi 164 instrument, using a 1 m x 3 mm glass column packed with 10% SE30 on Shimalite W. Oxidation and reduction potentials were measured in argon-saturated acetonitrile solutions by cyclic voltammetry, using a Nichia NP-G 2550 potentiostat and an Ag/AgCl reference electrode. Tetrabuthylammonium perchlorate (0.1 mol dm$^{-3}$) was used as a supporting electrolyte. Substituted 1,4-dicyanonaphthalenes were prepared according to the methods described in the literatures.[10] Spectoroscopic and analytical data are described as follows.

**1,4-Dicyano-2-methylnaphthalene** (2-MDCN): mp 198-200 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 2.80 (s, 3H), 7.76 (s, 1H), 7.77-7.85 (m, 2H), 8.27-8.32 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 21.08, 114.33, 114.61, 115.58, 116.35, 125.65, 125.75, 129.20, 130.23, 132.42, 133.55, 141.76; IR (KBr) 763, 903, 1166, 1376, 1510, 2224, 3066 cm$^{-1}$. Anal calcd for C$_{13}$H$_8$N$_2$: C, 81.23; H, 4.16; N, 14.58. Found: C, 81.49; H, 3.92; N, 14.62.

**1,4-Dicyano-2,3-dimethylnaphthalene** (DMDCN): mp 263-265 °C (263.5 °C);[10b] $^1$H NMR (270MHz, CDCl$_3$) δ 2.74 (s, 6H), 7.72-7.76 (m, 2H), 8.20-8.24 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 19.52, 114.35, 116.14, 125.56, 129.20, 130.76, 141.80; IR (KBr) 768, 1386, 1504, 1578, 2224, 3002 cm$^{-1}$.

**9,10-Dicyano-1,2,3,4-tetrahydroanthracene** (CyDCN): mp 264-265 °C (263 °C);[10b] $^1$H NMR (270MHz, CDCl$_3$) δ 1.95-2.00 (m, 4H), 3.20-3.25 (m, 4H), 7.70-7.73 (m, 2H), 8.18-8.23 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 21.86, 29.16, 113.78, 115.58, 125.24, 129.10, 130.76, 142.44; IR (KBr) 774, 1158, 1247, 1427, 1504, 2222, 2876, 2944, 2962 cm$^{-1}$.

**1,4-Dicyano-2,3-diphenylnaphthalene** (DPDCN): mp 226-227.5 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 7.14-7.18 (m, 4H), 7.25-7.31 (m, 6H), 7.85-7.89 (m, 2H), 8.41-8.45 (m, 2H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 115.03, 116.00, 126.25, 128.25, 128.76, 130.01, 130.19, 131.57, 136.12, 145.60; IR (KBr) 702, 743, 772, 1354, 1493, 2226, 3034 cm$^{-1}$. Anal calcd for C$_{24}$H$_{14}$N$_2$: C, 87.25; H, 4.27; N, 8.48. Found: C, 87.18; H, 4.00; N, 8.17.

*General Procedure for the Photoreaction of Cyanonaphthalenes with Allyltrimethylsilane (1).* A solution of a cyanonaphthalene and excess allyltrimethylsilane in acetonitrile-methanol (4:1) was irradiated at ambient temperature with a 300 W high-pressure mercury lamp through Pyrex filter under argon atmosphere. When phenanthrene was used as an additive, phenanthrene was added 2 eq mol of cyanonaphthalene. The progress of the photoreaction was monitored by GLC. After consumption (>90%) of the cyanonaphthalene, the solvent was removed under reduced pressure, and the residue was analyzed by $^1$H NMR, from which the product ratio was determined by integration of the signals. The product(s) was isolated by column chromatography on silica gel. The results are summarized in Tables 1 and 2.

**3-Cyano-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene** (4):[5e] oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.54 (d, 1H, *J*=12.49 Hz), 1.65 (d, 1H, *J*=11.28 Hz), 1.71 (d, 1H, *J*=13.29 Hz), 1.78-1.86 (m, 1H), 1.99-2.09 (m, 1H), 2.73-2.82 (m, 1H), 3.07-3.15 (m, 1H), 3.35 (t, 1H, *J*=5.24 Hz), 3.63-3.67 (m, 1H), 7.19-7.46 (m, 4H);$^{13}$C NMR (67MHz, CDCl$_3$) δ 35.00, 35.44, 37.31, 39.95, 42.79, 44.15, 46.71, 122.49, 126.57, 127.26, 127.61, 135.11, 145.07; IR (neat) 756, 1456, 1487, 2232, 2858, 2942, 3024, 3072 cm$^{-1}$; MS *m/z* 127, 154, 195 (M$^+$, vw). HRMS calcd for C$_{14}$H$_{13}$N 195.1048, found 195.1077.

**7-Cyano-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene** (5): oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.28 (d, 1H, *J*=10.9 Hz), 1.87 (d, 1H, *J*=13.7 Hz), 2.51 (s, 1H), 2.45-2.55 (m, 1H), 2.72-2.82 (m, 1H), 2.90-3.00 (m, 1H) 3.40-3.52 (m, 2H) 3.58 (d, 1H, *J*=6.45 Hz), 6.99-7.25 (m, 4H); $^{13}$C NMR (67MHz, CDCl$_3$) δ 35.71,

36.15, 37.65, 38.84, 39.01, 42.74, 48.49, 120.77, 125.81, 126.41, 127.61, 140.06, 142.61; IR (neat) 758, 1458, 1489, 2238, 2862, 2948, 3024, 3072 cm$^{-1}$; MS $m/z$ 129, 154, 195 (M$^+$, vw). HRMS calcd for $C_{14}H_{13}N$ 195.1048, found 195.1069.

**3-Cyano-8-methyl-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene (6)**: oil; $^1$H NMR (270MHz, CDCl$_3$) δ 1.45 (d, 1H, $J$=12.69 Hz), 1.63 (dd, 1H, $J$=1.41, 11.48 Hz), 1.72 (s, 3H), 1.68-1.75 (m, 2H), 2,11-2.21 (m, 1H), 2.34 (t, 1H, $J$=9.07 Hz), 3.02-3.10 (m, 1H), 3.31 (t, 1H, $J$=5.14 Hz), 7.16-7.50 (m, 4H); $^{13}$C NMR (67MHz, CDCl$_3$) δ 20.93, 40.00, 40.28, 40.34, 42.40, 42.50, 44.54, 50.65, 121.12, 126.29, 126.68, 127.00, 127.06, 135.81, 144.28; IR (neat) 758, 1454, 2232, 2870, 2944, 3026, 3072 cm$^{-1}$; MS $m/z$ 141, 153, 168, 194, 209 (M$^+$, vw). HRMS calcd for $C_{15}H_{15}N$ 209.1204, found 209.1259.

**3-Cyano-6-methyl-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene (7)**: oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.57 (s, 3H), 1.55-1.68 (m, 3H), 1.70-1.72 (m, 1H), 1.88 (dd, 1H, $J$=9.78, 13.40 Hz), 2.80-2.89 (m, 1H), 3.06 (dd, 1H, $J$=8.46, 10.88 Hz), 3.61-3.66 (m, 1H), 7.22-7.49 (m, 4H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 23.76, 36.20, 37.47, 41.57, 42.48, 45.29, 46.97, 47.05, 122.35, 123.34, 126.15, 126.98, 127.20, 133.97, 136.99; IR (neat) 841, 1251, 1458, 2232, 2904, 2958, 3030, 3074 cm$^{-1}$; MS $m/z$ 141, 153, 168, 209 (M$^+$, vw). HRMS calcd for $C_{15}H_{15}N$ 209.1204, found 209.1198.

**3,10-Dicyano-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene (8)**: oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.54 (d, 1H, $J$=12.89 Hz), 1.65 (d, 1H, $J$=11.49 Hz), 1.78 (d, 1H, $J$=13.70 Hz), 1.95 (dt, 1H, $J$=4.33, 12.89 Hz), 2.11-2.22 (m, 1H), 2.85 (q, 1H, $J$=6.44 Hz), 3.16 (dd, 1H, $J$=8.76, 11.58 Hz), 3.71-3.73 (m, 1H), 3.91 (t, 1H, $J$=5.24 Hz), 7.32-7.70 (m, 3H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 34.48, 34.76, 36.03, 39.03, 41.41, 42.08, 45.96, 110.79, 117.50, 127.65, 130.74, 131.27, 136.68, 148.08; IR (neat) 704, 806, 1280, 1448, 1640, 2230, 2938 cm$^{-1}$. HRMS calcd for $C_{15}H_{12}N_2$ 220.1001, found 220.0959.

**7,8-Dicyano-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene (9a)**: mp 211.5-212 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.44 (dt, 1H, $J$=1.41, 11.69 Hz), 2.00 (d, 1H, $J$=13.69 Hz), 2.66-2.77 (m, 1H), 2.84 (s, 1H), 3.10-3.21 (m, 1H), 3.31 (dt, 1H, $J$=4.23, 8.81Hz), 3.71 (d, 1H, $J$=6.04 Hz), 3.80 (ddd, 1H, $J$=1.67, 4.23, 8.91 Hz), 7.07-7.35 (m, 4H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 34.71, 38.36, 41.42, 42.05, 43.33, 43.79, 48.45, 117.13, 119.79, 126.70, 127.11, 127.38, 128.38, 136.79, 140.27; IR (neat) 756, 768, 1033, 1491, 2236, 2868, 2948, 2986 cm$^{-1}$; MS $m/z$ 129, 152, 153, 179, 203, 220 (M$^+$). Anal calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.45; N, 12.72. Found: C, 81.54; H, 5.40; N, 12.53.

**6,7-Dicyano-3,4-benzotricyclo[3.3.1.0$^{2,7}$]-3-nonene (9b)**: mp 220-222 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.36-1.46 (m, 1H), 2.24 (d, 1H, $J$=3.96, 13.35 Hz), 2.31 (dd, 1H, $J$=3.96, 13.35 Hz), 2.49 (q, 1H, $J$=6.43 Hz), 2.70 (d, 1H, $J$=1.49 Hz), 2.72-2.79 (m, 1H), 3.62 (d, 1H, $J$=3.96 Hz), 4.05 (d, 1H, $J$=5.44 Hz), 7.27-7.38 (m, 4H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 29.19, 32.22, 37.57, 38.88, 42.10, 45.46, 117.41, 119.59, 123.48, 126.61, 127.93, 128.52, 132.57, 142.49; IR (neat) 760, 1487, 2240, 2856, 2928 cm$^{-1}$. HRMS calcd for $C_{15}H_{12}N_2$ 220.1001, found 220.1006.

**2-Allyl-3-cyanonaphthalene (9c)**: oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 3.73 (d, 2H, $J$=6.04), 5.13-5.23 (m, 2H), 5.98-6.13 (m, 1H), 7.50-7.63 (m, 2H), 7.73 (s, 1H), 7.80-7.85 (m, 2H), 8.21 (s, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 38.40, 96.19, 110.93, 117.66, 118.19, 127.02, 127.69, 128.11, 128.35, 129.12, 131.04, 135.05, 135.13, 137.49; IR (KBr) 750, 919, 1636, 2226, 2926 cm$^{-1}$; MS $m/z$ 140, 165, 176, 193 (M$^+$).

**1-Allyl-4-cyano-2-methylnaphthalene (10a)**: mp 45 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 2.49 (s, 3H), 3.86 (d, 2H, $J$=5.49 Hz), 4.86 (d, 1H, $J$=17.09 Hz), 5.06 (d, 1H, $J$=10.38 Hz), 5.95-6.05 (m, 1H), 7.58-7.61 (m, 2H), 7.75 (s, 1H), 8.04-8.07 (m, 1H), 8.19-8.23 (m, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 19.90, 32.92, 108.58, 116.49, 118.13, 124.64, 125.73, 127.16, 127.51, 131.37, 132.18, 133.55, 134.40,

135.47, 139.35; IR (KBr) 763, 915, 1377, 1513, 2222, 2928, 3076 cm$^{-1}$. HRMS calcd for $C_{15}H_{13}N$ 207.1048, found 207.0932.

**1-Allyl-1,4-dicyano-1,2-dihydro-3-methylnaphthalene** (**10b**), *cis*-**1-Allyl-1,4-dicyano-1,2-dihydro-2-methylnaphthalene** (**10c**): **10b** and **10c** were not separated by column chromatography on silica gel. oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.47 (d, 3H, $J$=7.32 Hz), 2.29 (s, 3H), 2.44 (d, 2H, $J$=7.93 Hz), 2.49 (d, 2H, $J$=6.71 Hz), 2.77 (d, 1H, $J$=17.09 Hz), 2.96 (d, 1H, $J$=17.70 Hz), 3.26 (m, 1H), 4.99 (d, 1H, $J$=17.09 Hz), 5.08-5.15 (m, 2H), 5.27 (d, 1H, $J$=10.37 Hz), 5.46-5.52 (m, 1H), 5.77-5.85 (m, 1H), 6.57 (d, 1H, $J$=3.03 Hz), 7.38-7.57 (m, 8H). HRMS calcd for $C_{16}H_{14}N_2$ 234.1157, found 234.1152.

**3,6-Dicyano-8-methyl-4,5-benzotricyclo[4.2.1.0$^{3,8}$]-4-nonene** (**10d**): mp 138-140 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.69 (dd, 1H, $J$=0.99, 11.87 Hz), 1.76 (s, 3H), 1.94 (d, 1H, $J$=12.36 Hz), 2.21 (d, 2H, $J$=12.36 Hz), 2.52-2.68 (m, 2H), 3.05-3.13 (m, 1H), 7.36-7.73 (m, 4H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 20.31, 39.53, 40.46, 42.60, 45.31, 45.76, 46.89, 50.47, 119.84, 120.98, 125.10, 127.04, 128.07, 129.08, 134.38, 136.95; IR (KBr) 770, 1456, 1489, 2236, 2876, 2960 cm$^{-1}$. HRMS calcd for $C_{16}H_{14}N_2$ 234.1157, found 234.1138.

*cis*- **and** *trans*-**1-Allyl-1,4-dicyano-1,4-dihydro-2,3-dimethylnaphthalene** (**11**): oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 2.04 (s, 3H), 2.09 (s, 6H), 2.10 (s, 3H), 2.73 (d, 2H, $J$=4.05 Hz), 2.78 (d, 2H, $J$=7.93 Hz), 4.43 (s, 1H), 4.52 (s, 1H), 4.86 (d, 1H, $J$=17.01 Hz), 4.96 (d, 1H, $J$=11.88 Hz), 4.97 (d, 1H, $J$=17.09 Hz), 5.13, (d, 1H, $J$=10.99 Hz), 5.42-5.54 (m, 1H), 5.44-5.51 (m, 1H), 7.35-7.47 (m, 8H). HRMS $C_{17}H_{16}N_2$ calcd for 248.1313, found 221.1225 ($C_{16}H_{15}N$ calcd for 221.1204).

**1-Allyl-4-cyano-2,3-diphenylnaphthalene** (**13**): mp 146 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 3.70-3.72 (m, 2H), 4.82 (dd, 1H, $J$=1.54, 17.40 Hz), 5.06 (d, 1H, $J$=10.37 Hz), 5.92-6.02 (m, 1H), 6.99-7.20 (m, 10H), 7.65-7.75 (m, 2H), 8.18 (d, 1H, $J$=7.94 Hz), 8.38 (d, 1H, $J$=6.72 Hz); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 34.84, 116.81, 125.87, 126.25, 127.12, 127.61, 127.67, 127.71, 128.39, 129.93, 130.17, 131.31, 136.22, 138.81, 139.55; IR (KBr) 702, 752, 1444, 1497, 2222, 2926, 3030, 3062 cm$^{-1}$. Anal calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.50; N, 4.06. Found: C, 90.29; H, 5.36; N, 3.70.

*cis*- **and** *trans*-**9-Allyl-9,10-dicyano-1,2,3,4,9,10-hexahydroanthracene** (**14**): oil; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.78-1.80 (m, 8H), 2.08-2.50 (m, 5H), 2.15-2.51 (m, 3H), 2.69 (d, 2H, $J$=7.32 Hz), 2.78 (d, 2H, $J$=7.93 Hz), 4.35 (s, 1H), 4.47 (s, 1H), 4.89 (d, 1H, $J$=18.31 Hz), 4.99 (d, 1H, $J$=17.09 Hz), 5.00 (d, 1H, $J$=10.99 Hz), 5.14 (d, 1H, $J$=8.54 Hz), 5.21-5.39 (m, 1H), 5.47-5.59 (m, 1H), 7.36-7.65 (m, 8H). HRMS $C_{19}H_{18}N_2$ calcd for 274.1470, found 274.1457.

*Preparation of 12.* The column chromatography of **11** on silica gel (eluent; hexane:dichloromethane=1:1) gave **12** in a quantitative yield.

**cis-1-Allyl-1,4-dicyano-1,2-dihydro-2,3-dimethylnaphthalene** (**12**): mp 126 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.09 (d, 3H, $J$=6.71 Hz), 2.33 (s, 3H), 2.54 (dd, 1H, $J$=7.32 Hz), 2.88 (dd, 2H, $J$=6.72, 14.03 Hz), 5.19-5.30 (m, 2H), 5.73-5.94 (m, 1H), 7.37-7.58 (m, 4H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 10.60, 21.54, 35.87, 40.89, 43.59, 109.70, 115.64, 120.88, 121.30, 125.58, 126.19, 128.50, 128.80, 129.14, 129.39, 129.93, 130.84; IR (KBr) 768, 936, 1002, 1433, 2224, 2942, 2984, 3082 cm$^{-1}$. Anal calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.03; H, 6.47; N, 11.10.

*Preparation of 15 from 12.* A dry acetonitrile solution (5 cm$^3$) of **12** (24.8 mg, 0.1 mmol) in the presence of NaOMe (5.4 mg, 0.1 mmol) was refluxed for 1 h under argon atmosphere and then the solvent was removed. The residue was chromatographed on silica gel. Elusion with hexane-dichloromethane gave 17.1 mg (77 %) of **15**.

**1-Allyl-4-cyano-2,3-dimethylnaphthalene** (**15**): mp 85-87 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 2.41

(s, 3H), 2.72 (s, 3H), 3.89 (d, 2H, J=5.50 Hz), 4.85 (d, 1H, J=17.09 Hz), 5.07 (d, 1H, J=9.76 Hz), 5.97-6.07 (m, 1H), 7.53-7.61 (m, 2H), 8.01 (d, 1H, J= 8.55 Hz), 8.19 (d, 1H, J=8.55 Hz); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 16.26, 20.35, 33.28, 108.81, 116.45, 117.94, 124.61, 125.59, 126.68, 127.20, 129.16, 131.47, 134.68. Anal calcd for C$_{16}$H$_{15}$N: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.46; H, 6.57; N, 6.43.

**9-Allyl-10-cyano-1,2,3,4-tetrahydroanthracene** (**16**): mp 220-225 °C; $^1$H NMR (270 MHz, CDCl$_3$) δ 1.88-1.93 (m, 4H), 2.92 (s, 2H), 3.23 (s, 2H), 3.84-3.87 (m, 2H), 4.83-4.90 (m, 1H), 5.05-5.09 (m, 1H), 5.93-6.08 (m, 1H), 7.50-7.61 (m, 2H), 8.00-8.03 (m, 1H), 8.17-8.21 (m, 1H); $^{13}$C NMR (67 MHz, CDCl$_3$) δ 22.09, 22.95, 27.06, 30.09, 32.35, 108.20, 116.39, 117.40, 124.49, 125.32, 126.54, 127.28, 130.52, 131.61, 134.24, 134.60, 138.76, 143.09; IR (KBr) 762, 930, 1506, 1568, 1636, 2218, 2866, 2944, 3064 cm$^{-1}$. HRMS C$_{18}$H$_{17}$N calcd for 247.1361, found 247.1409.

*General Procedure for the Photoreaction in the Presence of MeOD.* An acetonitrile-methanol-O-d$_1$ (6:1) solution of mono- or dicyanonaphthalene (0.2 mmol) and **1** (0.6 mmol) was irradiated through Pyrex filter. Flash chromatography on silica gel gave the deuterated compounds **4-d$_1$**, **5-d$_1$**, **9a-d$_1$** and **9b-d$_1$**. In these deuterated compounds, the following changes were observed in their $^1$H NMR spectra. $^1$H NMR spectra of the deuterated compounds changed as follows. The signal at δ 1.54 of **4** almost disappeared in **4-d$_1$**. The signal at δ 2.51 of **5** almost disappeared in **5-d$_1$**. The signal at δ 2.84 of **9a** almost disappeared in **9a-d$_1$**. The signal at δ 2.70 of **9b** almost disappeared in **9b-d$_1$**.

*Triplet Sensitized Photoreaction of 2.* An acetonitrile solution of **2** (10 mmol dm$^{-3}$) containing Michler's ketone (30 mmol dm$^{-3}$), benzophenone (30 mmol dm$^{-3}$) or 2-methyl-1,3-butadiene (1 mol dm$^{-3}$) was irradiated in a merry-go-round apparatus through Pyrex filter under Ar. The progress of the photoreaction was monitored by GLC and the yield of **3** was determined.

*Quantum Yield from 2 to 3.* Quantum yields were determinded by the procedure of Murov[12] using a potassium ferrioxalate actinometer. The light intensity (313 nm light) was determined twice before and once after actual photoreactions. No change in light intensity was observed during experiments. For the quantum yields determination, photoreactions were carried out up to < 10 % conversion of **2** and the reaction mixtures were analyzed by GLC.

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