Photoamination of Alkenylnaphthalenes with Ammonia via Electron Transfer

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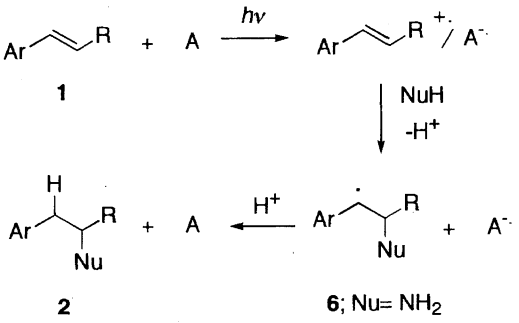
The photoamination of 1-(2-methyl-1-propenyl)naphthalene (**1a**) with ammonia in the presence of *p*-dicyanobenzene (*p*-DCB) occurred selectively at the alkenyl group but not at the naphthyl group to give 1-(2-amino-2-methylpropyl)naphthalene (**2a**). Similarly, the photoamination of several kinds of alkenylnaphthalenes (**1**) proceeded selectively at the alkenyl group. The photoamination proceeded via the nucleophilic addition of ammonia to the cation radical of **1** generated by the photoinduced electron transfer to *p*-DCB to give the aminated radical after deprotonation. Distribution of the positive charge in $\mathbf{1}^{+\bullet}$ and the stabilities of the aminated radicals were calculated by the PM3-UHF method. The stabilities of the aminated radicals agreed with the regioselectivity.

Photoinduced electron transfer (PET) has provided a variety of organic reactions applicable to organic synthesis. The most typical reaction of PET is photoinduced nucleophilic addition (PNA) to double bonds, which occurs through generation of the cation radicals of the substrates by PET to an electron acceptor and subsequent addition of nucleophiles to the cation radicals followed by electron transfer and protonation steps (see Scheme 1).[1] The PNA of MeOH provides useful mechanistic information in the reaction with 1, 1-diphenyl-1-alkenes,[2] styrenes,[3] and cyclopropanes,[4] but has been synthetically restricted since the PNA of MeOH could not be used on the extensively conjugated substrates. On the other hand, the PNA of ammonia and alkylamines (RNH_2) (photoamination) has provided a powerful method to introduce an amino group directly to C–C double bonds of a variety of substrates including stilbenes,[5] 1-aryl-1,3-alkadienes,[6] and polycyclic aromatic compounds,[7,8] which were inert to the PNA of MeOH, as well as arylalkenes,[9] since RNH_2 is a stronger nucleophile than MeOH. Here, we wish to report on the photoamination of alkenylnaphthalenes



Scheme 1.

(**1**), which contain reaction sites on both the polycyclic aromatic ring and the olefinic group, in order to examine factors controlling the regioselectivity of the photoamination of the extensively conjugated cation radicals.

Results and Discussion

Oxidation potentials (E^{ox}) of **1** were low (<1.1 V vs. $Ag/AgNO_3$). Strong fluorescences of **1** were observed at λ_{max} = 362—390 nm and were quenched in MeCN at nearly diffusional-controlled rates by *p*-dicyanobenzene (*p*-DCB) acting as an electron acceptor, but not by NH_3. The free energy changes for the electron transfer from the excited singlet state of **1** to *p*-DCB were calculated to be substantially negative by the Rehm–Weller equation[10] using E^{ox} and singlet energy (E^{O-O}). Therefore, the photoamination according to Scheme 1 (A = *p*-DCB and NuH = NH_3) will be realized in **1** in polar solvents. These parameters are summarized in Table 1.

The photoamination of **1** was done by irradiation of an ammonia-saturated MeCN–H_2O (8 : 2 v/v) solution containing **1** and *p*-DCB by a high-pressure mercury lamp through a Pyrex filter. After the photoreaction, the aminated products (**2**) were acetylated by Ac_2O and then isolated by column chromatography on silica gel. The products and yields are shown in Table 2. The photoamination of 1-(2-methyl-1-propenyl)naphthalene (**1a**) occurred selectively at the alkenyl group to give 1-(2-amino-2-methylpropyl)naphthalene (**2a**). The photoamination of 1-styrylnaphthalene (**1b**) gave 1-(2-amino-2-phenylethyl)naphthalene (**2b**). Also, the photoamination of 2-naphthyl isomers (**1c,d**) occurred selectively at alkenyl groups to give **2c** and **2d**, respectively (Scheme 2). Irradiation of **1a** and **1b** for a long time under the photoamination conditions gave 1-methylnaphthalene (**3a**) as a conse-

Table 1. Fluorescence Quenching Data and Oxidation Potentials of **1**

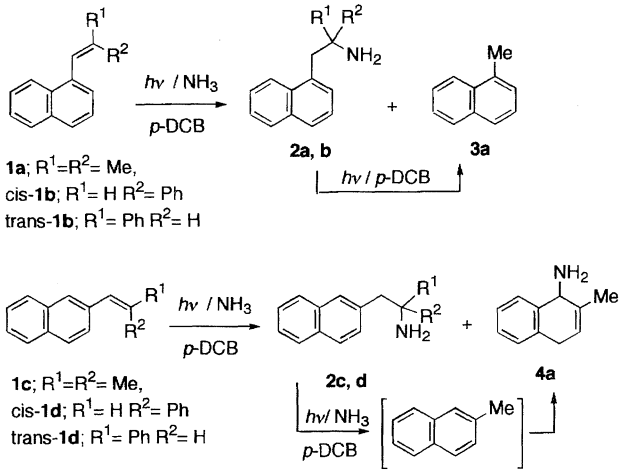
1	$E_{1/2}^{ox}$ a)	E^{O-O} b)	τ_F c)	K_{sv} d)	k_q e)	ΔG f)
	V	kJ mol^{-1}	ns	M^{-1} g)	10^{10} M^{-1} s^{-1}	kJ mol^{-1}
1a	1.08	330	5	93	1.9	−43
***trans*-1b**	0.95	307	3	73	2.4	−32
1c	0.91	328	33	402	1.2	−57
***trans*-1d**	1.01	315	16	123	0.8	−34
1e	0.84	318	11	234	2.1	−54
1f	0.90	319	2	49	2.2	−48
5a	1.40	285	10	<5	<0.1	29
5b	1.67	261	1	< 5	<0.5	79
5c	1.04	257	9	< 5	<0.5	15
5d	1.29	243	2	< 5	<0.5	59

a) Half peak of oxidation potentials vs. Ag/$AgNO_3$. b) Excitation energy for the excited singlet states of **1** were estimated from the fluorescence maxima since no fine structure was observed. c) Lifetime of fluorescence. d) Stern–Volmer constants for fluorescence quenching of **1** by *p*-DCB. e) Rate constants for the fluorescence quenching. f) Free energy change for the electron transfer from the excited singlet state of **1** to *p*-DCB ($E_{1/2}^{red} = -1.96$ V) calculated by Rehm–Weller equation (see Ref. 10). g) 1 M = 1 mol dm^{-3}.

Table 2. Photoamination of **1**[a)]

1	t[b)]	Product (Yield/%)	Conv.	Recov. of
	h		of **1** (%)	DCB (%)
1a	4	**2a** (45)	46	73
1a	8	**2a** (22) **3a** (6)	100	75
***cis*-1b**	7	**2b** (67)	100	63
***trans*-1b**	7	**2b** (40)	100	68
***trans*-1b**	10	**2b** (27) **3a** (10)	100	43
1c	1	**2c** (64)	100	84
1c	4	**2c** (62) **4a** (12)	100	77
***cis*-1d**	7	**2d** (54)	100	94
***trans*-1d**	3	**2d** (29)	100	86
1e	3	**2e** (15) **3b** (18) **4b** (30)	97	84

a) For an ammonia-saturated MeCN–H_2O (8 : 2, 70 ml) solution containing **1** (3.5 mmol) and *p*-DCB (3.5 mmol). b) Irradiation time.

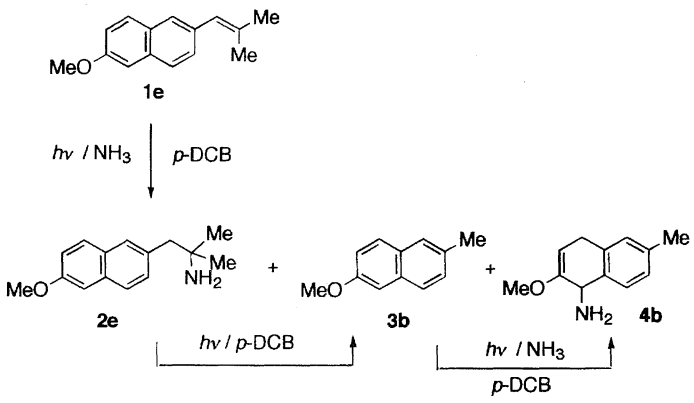


Scheme 2.

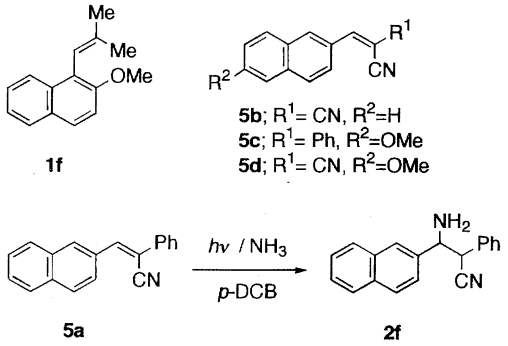
quence of β-fission of the amino groups of **2a** and **2b**, as has been reported for β-fission of phenylethyl alkyl ethers and 1-(2-aminoethyl)naphthalenes via electron transfer.[11] In the case of **1c**, irradiation for a long time gave 1-amino-2-methyl-1,4-dihydronaphthalene (**4a**), which would be produced by the photoamination of 2-methylnaphthalene formed by the decomposition of **2c**.[7] The photoaminations of *cis*-**1b** and *cis*-**1d** proceeded in higher yields than those of their *trans*-isomers. For example, the photoaminations of *cis*- and *trans*-**1b** gave **2b** in 67 and 40% yields, respectively.

Moreover, the photoamination of **1e**,**f**, which have a methoxy group on the aromatic ring was investigated, since the methoxy group can strongly affect the distribution of the positive charge in the cation radicals.[12] The photoamination of 6-methoxy-2-(2-methyl-1-propenyl)naphthalene (**1e**) occurred at the alkenyl group to give 2-(2-amino-2-methylpropyl)-6-methoxynaphthalene (**2e**) along with the formations of 2-methoxy-6-methylnaphthalene (**3b**) and 1-amino-2-methoxy-6-methyl-1,4-dihydronaphthalene (**4b**) as secondary products (Scheme 3). On the other hand, no photoamination of 2-methoxy-1-(2-methyl-1-propenyl)naphthalene (**1f**) occurred at either the alkenyl group or the naphthalene ring, so **1f** was recovered in 86% yield after irradiation for 8 h.

The photoamination of **5a**—**d**, which was substituted by



Scheme 3.



Scheme 4.

a cyano group at the alkenyl groups afforded little or no aminated products (Scheme 4). The photoamination of **5a** occurred at the benzylic position to give **2f** in 3% yield. The fluorescences of **5a—d** were quenched by DCB inefficiently and were very weak compared with those of **1a—f** due to the occurrence of the intramolecular charge transfer quenching between the naphthalene ring and the mono- and dicyanoethene moieties (Table 1). A Rehm–Weller calculation showed that the free energy changes for electron transfer from ^{1}**5*** to *p*-DCB were endoergic in the cases of **5**. This is a reason why no photoamination of **5a—d** occurred.

PM3 Calculation. As mentioned above, the photoamination proceeded via the nucleophilic addition of NH_3 to $\mathbf{1}^{+\bullet}$ generated by photoinduced electron transfer to *p*-DCB to give the aminated cation radical and the anion radical of *p*-DCB (*p*-DCB$^{-\bullet}$). The aminated cation radical was deprotonated to give the aminated radical (**6**) which was reduced by *p*-DCB$^{-\bullet}$ and then protonated to give **2**. Therefore, the nucleophilic addition of NH_3 to $\mathbf{1}^{+\bullet}$ should be a key pathway deciding the regiochemistry. The rates of the nucleophilic addition should depend on both the positive charge density of the reaction site in $\mathbf{1}^{+\bullet}$ and the stabilities of **6**. Therefore, we deduced these values by semi-empirical PM3 calculation on MOPAC.[13]

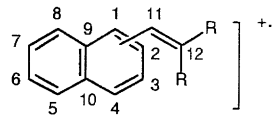
Table 3 shows the distribution of the positive charge of $\mathbf{1a—d}^{+\bullet}$ calculated by PM3-UHF. The positive charge of $\mathbf{1a}^{+\bullet}$ and *trans*-$\mathbf{1b}^{+\bullet}$ were distributed over C-1 and C-4 of the naphthalene ring and the β-position (C-12) of the alkenyl group. In the cation radicals of 2-naphthyl derivatives (**1c** and **1d**), the positive charge developed over C-1, C-2, and C-12. In the cases of $\mathbf{1e}^{+\bullet}$ and $\mathbf{1f}^{+\bullet}$, the PM3-calculation showed that the positive charge was distributed mainly on the respective C-6 and C-2 substituted by a MeO group, but little at C-12 where the photoamination actually occurred (Table 4). Also the calculation by GAUSSIAN-92 (ab initio molecular orbital calculation)[14] showed that the highest positive charge was not at C-12 (Table 4). Thus, the calculation showed that the positive charge of $\mathbf{1a—e}^{+\bullet}$ were delocalized over both the naphthalene ring and alkenyl group, showing that the charge distribution cannot be directly related to the regioselective photoamination on C-12.

The difference in the heat formation (H_a) between the aminated radicals is thought to be equal to the difference in the stabilities of the aminated radicals. Therefore, the

Table 3. Total Charge Distribution of the Cation Radicals of **1a—d** Calculated by PM3-UHF Method[a]

Position	**1a**	*trans*-**1b**[b]	**1c**	*trans*-**1d**[c]
Total-H[d]	1.05	1.04	1.13	1.12
C1	0.13	0.05	0.02	0.02
C2	−0.07	−0.05	0.09	0.00
C3	−0.07	−0.09	−0.16	−0.12
C4	0.06	0.04	0.03	−0.02
C5	−0.04	−0.05	−0.05	−0.08
C6	−0.06	−0.07	−0.02	−0.03
C7	−0.04	−0.04	−0.08	−0.08
C8	−0.05	−0.08	−0.04	−0.06
C9	−0.05	−0.03	−0.08	−0.06
C10	−0.08	−0.07	−0.02	0.00
C11	−0.14	−0.07	−0.12	−0.02
C12	0.12	0.07	0.13	0.06

a) The numbering was performed as follows:

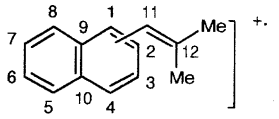


b) The charge on the phenyl group is +0.241. c) The charge on the phenyl group is +0.267. d) Summation of positive charge of hydrogens on C-1 to C-12.

Table 4. Charge Distribution of the Cation Radicals of **1e—f** Calculated by PM3 and GAUSSIAN 92[a]

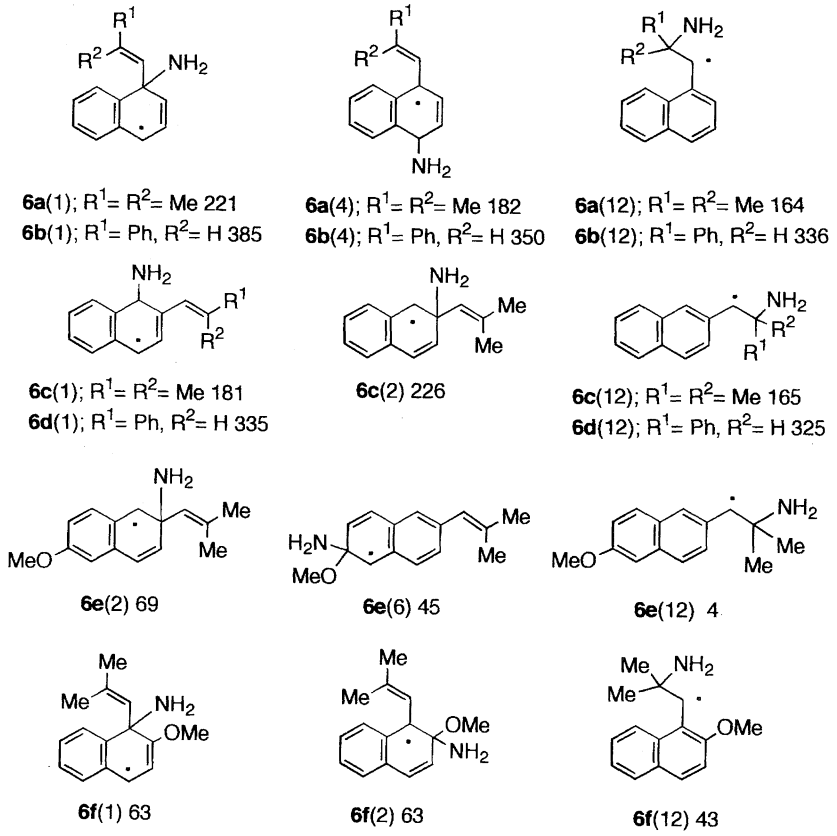
Position	**1e**		**1f**	
	PM3	GAUSSIAN	PM3	GAUSSIAN
Total-H[b]	0.92	0.93	0.94	0.94
C1	0.05	−0.24	0.05	0.29
C2	0.06	0.26	0.25	0.35
C3	−0.136	−0.38	−0.26	−0.15
C4	0.00	0.21	0.12	−0.04
C5	−0.08	0.15	−0.03	−0.31
C6	0.22	0.33	−0.06	0.17
C7	−0.21	−0.16	−0.04	−0.37
C8	0.06	−0.03	−0.07	0.21
C9	−0.12	0.13	−0.05	−0.28
C10	0.00	−0.22	−0.10	0.17
C11	−0.15	−0.37	−0.14	−0.35
C12	0.05	0.33	0.06	0.29

a) The numbering was performed as follows:



b) Summation of positive charge of hydrogens on C-1 to C-12.

PM3-UHF calculation of H_a was done for selected aminated radicals (**6**(n); the term n refers to the amination site, n = 1,2,4,6,12) derived from the nucleophilic addition of NH_3 to the positive sites of $\mathbf{1}^{+\bullet}$. In the case of **1a**, for example, the calculation was done for three kinds of radicals (**6a**(n)) aminated to the positive center at C-1, C-4, and C-12 of $\mathbf{1a}^{+\bullet}$. The **6a**(12), which is an intermediate to give **2a**, is most stable among the **6**(n), thus showing that the regioselectivity of the



Scheme 5. PM3-calculation of the heat formation of the selected aminated radicals (in kJ mol^{-1}).

photoamination of **1a** is related to the stability of the aminated radicals. Similarly, PM3-calculation in **1b—e** showed that the $H_a$values of **6**(12) were much lower than those of other isomeric aminated radicals (**6**(*n*); $n \neq 12$), demonstrating that the photoamination proceeded via the most stable aminated radical (Scheme 5).

In the case of **1f**, no photoamination occurred, although Table 1 suggests strongly the generation of $\mathbf{1f}^{+\cdot}$ by the photoinduced electron transfer from **1f** to *p*-DCB. However, we cannot explain clearly a reason why $\mathbf{1f}^{+\cdot}$ was inert to NH_3. Probably the nucleophilic addition of NH_3 at C-12 is sterically unfavorable, since the alkenyl group is not co-planar with the naphthyl ring and the C-1 position is crowded. The calculation by GAUSSIAN-92 showed that the torsional angle between naphthyl ring and 2-methyl-1-propenyl group was 47°.

We concluded that the photoamination proceeded via the most stable aminated radical. As has been reported for the photonucleophilic addition of 1-phenyl-1,3-alkadiene, 1,4-diphenyl-1,3-butadiene,[6] and simple 1,3-alkadienes,[15] the regiochemistry of the photoamination was, to some extent, related to the PM3-calculated positive-charge distribution of the cation radicals. However, in the case of **1** containing a polycyclic aromatic ring such as naphthalene ring, it is difficult to relate the amination site to the distribution of the positive charge, since the positive charge delocalizes extensively over the molecule.

Experimental

Melting points were measured on a Shibata MEL 270 and were uncorrected. ^1H and ^{13}C NMR spectra were taken on a Bruker AC 250P spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi 2000A spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorometer. The oxidation potentials were measured by cyclic voltammetry for a MeCN solution containing Et_4BF_4 (0.1 mol dm^{-3}) at a scan rate of 0.5 V s^{-1} on a Hokuto Denko HA-501G and HB-105 as a potentiostat and function generator using $Ag/AgNO_3$ as a reference electrode.

Materials. Acetonitrile of spectral grade was distilled from CaH_2 before use. *p*-DCB were recrystallized from MeOH. Compounds **1a—f** were prepared by Wittig reactions of 1- and 2-naphthaldehydes with isopropyl- and benzyltriphenylphosphonium chlorides in the presence of BuLi in tetrahydrofuran. Compounds **5a—d** were prepared by the reaction of 2-naphthaldehyde and 6-methoxy-2-naphthaldehyde with fumaronitrile and phenylacetonitrile in the presence of EtONa.

1-(2-Methyl-1-propenyl)naphthalene (1a). ^1H NMR δ = 1.72 (s, 3H), 2.02 (s, 3H), 6.65 (s, 1H), 7.28 (d, J = 7.0 Hz, 1H), 7.29—7.48 (m, 3H), 7.71 (d, J = 8.2 Hz, 1H), 7.80—7.83 (m, 1H), 7.97—8.00 (m, 1H); ^{13}C NMR δ = 19.56, 26.14, 122.90, 125.23, 125.30, 125.55, 126.61, 128.27, 132.18, 133.55, 135.99, 136.68. HRMS Found: *m/z* 182.1060. Calcd for $C_{14}H_{14}$; M, 182.1094.

***trans*-1-Styrylnaphthalene (*trans*-1b).** Mp 70 °C (from MeOH); ^1H NMR δ = 6.81 (d, J = 12.2 Hz, 1H), 7.06 (s, 5H), 7.10—8.22 (m, 8H); ^{13}C NMR δ = 123.62, 123.77, 125.67, 125.81, 125.81, 126.07, 126.68, 127.76, 128.02, 128.60, 128.73, 131.41, 131.76, 133.73, 135.01, 137.62. HRMS Found: *m/z* 230.1085.

Calcd for $C_{18}H_{14}$: M, 230.1094.

***cis*-1-Styrylnaphthalene (*cis*-1b).** ^{1}H NMR δ = 6.90 (d, J = 12.2 Hz, 1H), 7.07 (s, 5H), 7.30—8.09 (m, 8H).

2-(2-Methyl-1-propenyl)naphthalene (1c). Oil; ^{1}H NMR δ = 1.91 (d, J = 1.2 Hz, 3H), 1.92 (d, J = 1.0 Hz, 3H), 6.40 (br s, 1H), 7.33—7.44 (m, 3H), 7.64 (s, 1H), 7.72—7.78 (m, 3H); ^{13}C NMR δ = 19.48, 26.88, 125.20, 125.29, 125.84, 127.04, 127.39, 127.51, 127.51, 127.74, 131.83, 133.44, 135.91, 136.21. HRMS Found: m/z 182.1055. Calcd for $C_{14}H_{14}$: M, 182.1094.

***trans*-2-Styrylnaphthalene (*trans*-1d).** ^{1}H NMR δ = 7.14—7.53 (m, 6H), 7.62—7.79 (m, 3H); ^{13}C NMR δ = 123.43, 125.11, 125.83, 126.27, 126.50, 126.62, 126.62, 127.95, 128.25, 128.42, 128.67, 128.93, 132.97, 133.63, 134.73, 137.27. HRMS Found: m/z 230.1121. Calcd for $C_{18}H_{14}$: M, 230.1095.

***cis*-2-Styrylnaphthalene (cis-1d).** ^{1}H NMR δ = 6.61 (d, J = 12.3 Hz, 1H), 6.66 (d, J = 12.3 Hz, 1H), 6.97—7.36 (m, 9H), 7.54—7.69 (m, 4H); ^{13}C NMR δ = 125.82, 125.93, 126.86, 127.17, 127.44, 127.55, 127.88, 127.97, 128.18, 128.92, 130.10, 130.51, 132.49, 133.40, 134.78, 137.15. HRMS Found: m/z 230.1191. Calcd for $C_{18}H_{14}$: M, 230.1095.

6-Methoxy-2-(2-methyl-1-propenyl)naphthalene (1e). ^{1}H NMR δ = 1.92 (d, J = 3.6 Hz, 3H), 2.12 (s, 3H), 3.87 (s, 3H), 6.37 (br s, 1H), 7.08 (s, 1H), 7.08—7.13 (m, 1H), 7.32 (dd, J = 8.5, 1.6 Hz, 1H), 7.58 (s, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ = 19.44, 26.85, 55.19, 105.60, 118.63, 125.12, 126.23, 126.89, 127.98, 128.86, 129.22, 132.81, 134.03, 135.17, 157.36. HRMS Found: m/z 212.1200. Calcd for $C_{15}H_{16}O$: M, 212.1200.

2-Methoxy-1-(2-methyl-1-propenyl)naphthalene (1f). ^{1}H NMR δ = 1.49 (d, J = 0.7 Hz, 3H), 2.05 (d, J = 1.2 Hz, 3H), 3.88 (s, 3H), 6.34 (br s, 1H), 7.22—7.45 (m, 3H), 7.72—7.85 (m, 3H); ^{13}C NMR δ = 20.36, 25.94, 56.51, 113.44, 118.41, 121.59, 123.47, 125.34, 126.17, 128.19, 128.35, 129.08, 133.21, 138.22, 154.18. HRMS Found: m/z 212.1160. Calcd for $C_{15}H_{16}O$: M, 212.1200.

2-(2-Cyanostyryl)naphthalene (5a). ^{1}H NMR δ = 7.21—8.29 (m, 13H); ^{13}C NMR δ = 111.40, 123.10, 125.15, 125.90, 126.72, 127.57, 127.67, 128.61, 128.69, 129.00, 129.11, 130.38, 131.13, 132.98, 134.00, 134.48, 142.10. HRMS Found: m/z 255.1059. Calcd for $C_{19}H_{13}N$: M, 255.1047.

2-(2,2-Dicyanoethenyl)naphthalene (5b). ^{1}H NMR δ = 7.57—7.71 (m, 3H), 7.99 (s, 1H), 7.92—8.08 (m, 3H), 7.87 (s, 1H); ^{13}C NMR δ = 82.21, 112.81, 113.94, 124.16, 127.66, 127.98, 128.50, 129.62, 129.62, 129.94, 132.57, 134.37, 135.83, 159.67. IR 2240 cm^{-1}, HRMS Found: m/z 204.0660. Calcd for $C_{14}H_8N_2$: M, 204.0686.

2-(2-Cyanostyryl)-6-methoxynaphthalene (5c). Mp 132—133 °C (from MeOH); ^{1}H NMR δ = 3.94 (s, 3H), 7.14—7.20 (m, 2H), 7.24—7.49 (m, 3H), 7.62—7.80 (m, 5H), 8.08 (d, J = 8.7 Hz, 1H), 8.20 (s, 1H); ^{13}C NMR δ = 55.24, 105.72, 109.86, 118.36, 119.54, 125.72, 125.72, 127.30, 128.34, 128.81, 128.81, 128.91, 130.23, 130.33, 134.62, 135.51, 142.21, 159.05. HRMS Found: m/z 285.1203. Calcd for $C_{20}H_{15}NO$: M, 285.1153.

2-(2,2-Dicyanoethenyl)-6-methoxynaphthalene (5d). Mp 184—185 °C (from MeOH); ^{1}H NMR δ = 3.97 (s, 3H), 7.16—7.26 (m, 2H), 7.70—7.88 (m, 3H), 8.06 (d, J = 8.9 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR δ = 54.80, 82.21, 105.42, 112.81, 113.94, 119.72, 124.08, 125.50, 127.00, 127.34, 130.59, 133.95, 137.00, 159.45, 160.00. HRMS Found: m/z 234.0786. Calcd for $C_{15}H_{10}N_2O$: M, 234.0792.

General Procedure of Photoamination. An MeCN–H_2O (8 : 2, v/v, 70 ml) solution containing **1** (3.5 mmol) and *p*-DCB (3.5 mmol) was introduced into a Pyrex vessel. Gaseous NH_3 was bubbled through the solution for 20 min, after which it was irradiated with an Eikosha PIH-300 high-pressure mercury lamp (300 W) for 1—10 h with water cooling. After the photoreaction, the mixture was evaporated under reduced pressure. The photolysates were treated with acetic anhydride (10 ml), and then treated with saturated aqueous $NaHCO_3$ with ice cooling. The reaction mixture was then extracted with $CHCl_3$ and the extract was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ as eluent. After the elution of **1** and DCB, the aminated products were isolated as the acetamides. ^{1}H NMR spectroscopy showed that the purity of the aminated products were >90%.

1-(2-Amino-2-methylpropyl)naphthalene (2a). The acetamide. ^{1}H NMR δ = 1.34 (s, 6H), 1.83 (s, 3H), 3.54 (s, 2H), 5.33 (br s, 1H), 7.24—7.51 (m, 4H), 7.72 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ = 24.50, 27.76, 40.12, 54.95, 124.72, 124.96, 125.27, 125.58, 127.07, 128.53, 128.90, 133.23, 133.79, 134.54, 169.96. HRMS Found: m/z 241.1436. Calcd for $C_{16}H_{19}NO$: M, 241.1465.

1-(2-Amino-2-phenylethyl)naphthalene (2b). The acetamide. Mp 177 °C (from EtOH); ^{1}H NMR δ = 1.93 (s, 3H), 3.41 (dd, J = 13.9, 7.8 Hz, 1H), 3.72 (dd, J = 13.9, 6.6 Hz, 1H), 5.38 (q, J = 7.4 Hz, 1H), 5.91 (br d, 1H), 6.98 (d, J = 7.0 Hz, 1H), 7.16—7.72 (m, 6H), 7.40—7.57 (m, 2H), 7.68 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ = 23.10, 39.77, 54.37, 125.01, 125.49, 126.10, 126.37, 126.58, 127.19, 127.31, 128.44, 128.62, 129.10, 132.10, 133.52, 133.66, 141.57, 169.56. HRMS Found: m/z 289.1445. Calcd for $C_{20}H_{19}NO$: M, 289.1465.

2-(2-Amino-2-methylpropyl)naphthalene (2c). The acetamide. Mp 121 °C (from EtOH); ^{1}H NMR δ = 1.36 (s, 6H), 1.90 (s, 3H), 3.21 (s, 2H), 5.12 (s, 1H), 7.21—7.77 (m, 6H); ^{13}C NMR δ = 24.48, 27.46, 44.51, 54.25, 125.37, 125.86, 126.67, 127.23, 127.51, 128.86, 129.04, 132.11, 132.69, 133.29, 135.69, 169.91. HRMS Found: m/z 241.1466. Calcd for $C_{16}H_{19}NO$: M, 241.1502.

2-(2-Amino-2-phenylethyl)naphthalene (2d). The acetamide. Mp 70 °C (from $CHCl_3$); ^{1}H NMR δ = 1.85 (s, 3H), 3.17 (dd, J = 14.0, 7.0 Hz, 1H), 3.26 (dd, J = 14.0, 7.0 Hz, 1H), 5.33 (m, 1H), 6.77 (br s, 1H), 7.05—7.77 (m, 12H); ^{13}C NMR δ = 22.92, 42.57, 54.77, 125.43, 125.89, 126.64, 127.38, 127.46, 127.52, 127.77, 128.29, 128.51, 129.21, 132.15, 133.29, 134.93, 141.39, 169.81. HRMS Found: m/z 289.1489. Calcd for $C_{20}H_{19}NO$: M, 289.1466.

2-(2-Amino-2-methylpropyl)-6-methoxynaphthalene (2e). The acetamide. ^{1}H NMR δ = 1.31 (s, 6H), 1.86 (s, 3H), 3.21 (s, 2H), 3.86 (s, 3H), 5.46 (br s, 1H), 7.07—7.25 (m, 3H), 7.47 (s, 1H), 7.60—7.65 (m, 2H); ^{13}C NMR δ = 24.17, 27.16, 44.19, 54.05, 55.04, 105.35, 118.47, 125.95, 128.50, 128.62, 128.84, 129.37, 132.98, 133.17, 157.12, 169.91. HRMS Found: m/z 271.1598. Calcd for $C_{17}H_{21}NO_2$: M, 271.1572.

2-(1-Amino-2-cyano-2-phenylethyl)naphthalene (2f). The acetamide. Mp 180 °C (from $CHCl_3$); ^{1}H NMR δ = 2.11 (s, 3H), 4.88 (d, J = 5.1 Hz, 1H), 5.38 (dd, J = 7.2, 5.1 Hz, 1H), 6.48 (d, J = 7.2 Hz, 1H), 7.00—7.98 (m, 12H); ^{13}C NMR δ = 22.42, 42.59, 56.72, 117.97, 124.06, 125.64, 126.00, 126.71, 127.21, 127.53, 127.62, 129.28, 130.92, 131.69, 169.52.

2-Methoxy-6-methylnaphthalene (3b). ^{1}H NMR δ = 2.45 (s, 3H), 3.86 (s, 3H), 7.08 (s, 1H), 7.08—7.30 (m, 2H), 7.51 (s, 1H), 7.62 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ = 21.42, 55.21, 105.68, 118.60, 126.58, 126.70, 128.57, 128.70, 129.16, 132.67, 132.99, 157.07. HRMS Found: m/z 172.0887. Calcd for $C_{12}H_{12}O$: M, 172.0903.

1-Amino-2-methyl-1,4-dihydronaphthalene (4a).[7] The acetamide. ^{1}H NMR δ = 1.82 (d, J = 1.7 Hz, 3H), 1.98 (d, J = 2.7 Hz, 3H), 3.35—3.38 (m, 2H), 5.60—5.75 (m, 2H), 5.80 (br s, 2H),

7.11—7.21 (m, 3H), 7.36—7.40 (m, 1H); ^{13}C NMR δ = 20.49, 23.20, 29.68, 49.08, 122.80, 126.56, 126.99, 127.81, 128.78, 132.31, 133.88, 135.51, 169.56. HRMS Found: *m/z* 201.1152. Calcd for $C_{13}H_{15}NO$: M, 201.1181.

1-Amino-2-methoxy-6-methyl-1,4-dihydronaphthalene (4b). The acetamide. ^{1}H NMR δ = 1.98 (d, J = 2.4 Hz, 3H), 2.31 (s, 3H), 3.42—3.48 (m, 2H), 3.59 (s, 3H), 5.00 (t, J = 3.6 Hz, 1H), 5.77 (s, 2H), 6.96 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ = 20.93, 23.37, 28.60, 47.43, 54.43, 94.21, 127.45, 128.03, 128.68, 132.53, 133.79, 136.73, 152.54, 169.67. HRMS Found: *m/z* 231.1257. Calcd for $C_{14}H_{17}NO_2$: M, 231.1216.

Calculation of the Cation Radicals of 1. The PM3-calculation was done on a Silicon Graphics Indigo 2 IRIS workstation using Daikin MOL-MOLIS/CRYS ver. 2.0 and MOPAC ver. 6 at Material Research Center of Miyazaki University. The calculation on $\mathbf{1}^{+\bullet}$ was done by PM3-UHF to give the structure with minimum energy and the distribution of charge. The HF/3-21G calculations were done using GAUSSIAN 92 at CONVEX C3440 in the Computer Center of Ehime University.

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