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Redox-photosensitized amination of alkenes and alkadienes with ammonia and alkylamines

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Abstract—Using 1,2,4-triphenylbenzene as a photosensitizer, the photoamination of alkenes and alkadienes (**1**), which had no absorption at >300 nm proceeded efficiently in the presence of *p*-dicyanobenzene to give addition products by incorporating both amino and *p*-cyanophenyl groups. The reaction efficiency was discussed in terms of the relationships between **1** and the photosensitizer in their oxidation potentials and the distribution of positive charge on the reaction site of the cation radical of **1** ($\mathbf{1}^{+\bullet}$).

1. Introduction

Ammonia is the simplest nitrogen source in biological and industrial syntheses. However, the common direct amination to C–C double bond using ammonia has been scarcely reported. Photochemical reactions make it possible for direct amination with ammonia to provide a more convenient synthetic method.[1] We have successfully achieved the direct amination of arenes and aryl-substituted alkenes by the nucleophilic addition of ammonia to the cation radicals of the substrates generated by photoinduced electron transfer.[2–7] However, simple alkenes are different from highly conjugated system such as arenes and aryl-substituted alkenes in the photoreactivity, because simple alkenes have relatively higher oxidation potentials, no aromatic groups stabilizing their cation radicals, and weak absorption at near UV region. For the photoinduced nucleophilic addition of MeOH to simple alkenes, Arnold and his co-workers have proposed a photo-NOCAS (photochemical nucleophile–olefin combination, aromatic substitution) reaction by photosensitization using biphenyl and *p*-dicyanobenzene (DCB) system.[8] Herein, we will report on the photo-NOCAS type reaction of simple alkenes and alkadienes using ammonia and alkylamines as nucleophiles.

2. Results and discussion

2.1. Product analysis

Redox-photosensitization was applied to the photoamination of simple alkenes and alkadienes (**1**), which had no absorption at >300 nm (Chart 1). The redox-photosensitization[9] generates a cation radical of **1** ($\mathbf{1}^{+\bullet}$) by the hole transfer from the cation radical of a sensitizer ($S^{+\bullet}$) generated by the photoinduced electron transfer, as shown in Scheme 1. In the present redox-photosensitized amination, 1,2,4-triphenylbenzene (TPB) and 2,2′-methylenedioxy-1,1′-binaphthalene (BN) were used as sensitizers since TPB and BN have higher

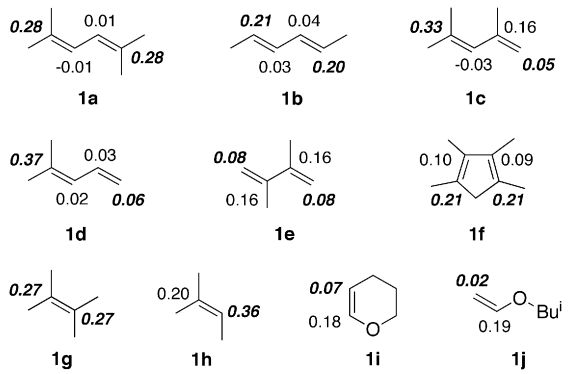

Chart 1. The alkadienes (**1a–f**) and alkenes (**1g–j**) for photoamination. The values are charge distribution on the carbon atom of the cation radicals of **1** calculated by ab initio method. The values given in bold italics correspond to the amination sites.

Keywords: Redox-photosensitization; Photoamination; Addition reaction; Electron-transfer.
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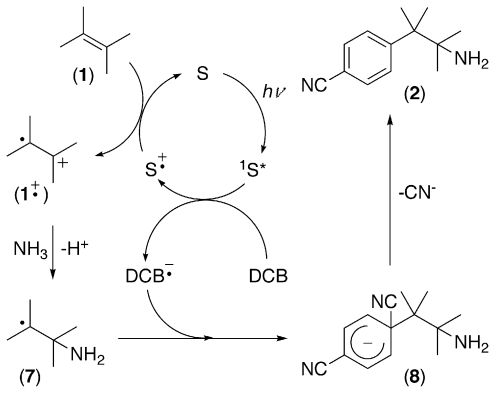
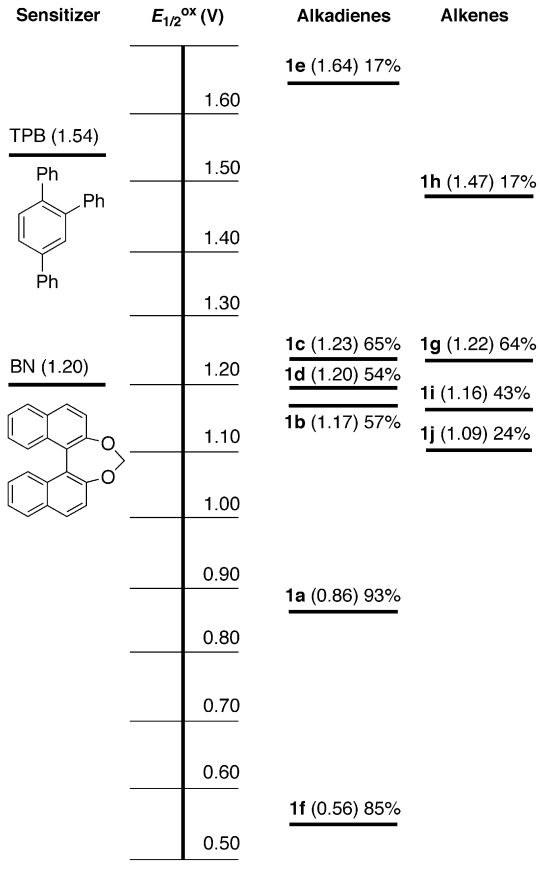


Scheme 1. Redox-photosensitization.

oxidation potentials ($E^{ox}_{1/2}$ vs $Ag/AgNO_3$) than those of most of **1** (Scheme 2) and were inert toward the nucleophilic attack of ammonia and alkylamines.[10] *p*-Dicyanobenzene (DCB) was used as an electron acceptor for the present photoamination in order to isolate the photo-NOCAS type products.



Scheme 2. Relationship between the oxidation potentials of **1a–j** and those of sensitizers.

The TPB-photosensitized amination of 2,5-dimethyl-2,4-hexadiene (**1a**) with NH_3 was carried out by irradiation of an ammonia-saturated MeCN–H_2O solution (v/v, 19:1, 70 mL) containing **1a** (7 mmol), DCB (3.5 mmol), and TPB (1 mmol) by a high-pressure Hg lamp through a Pyrex filter. (*E*)-4-(4-Amino-1,1,4-trimethyl-2-pentenyl)benzonitrile (**2a**) incorporating both amino and *p*-cyanophenyl groups into 1,4-positions of **1a** was formed in a 79% yield

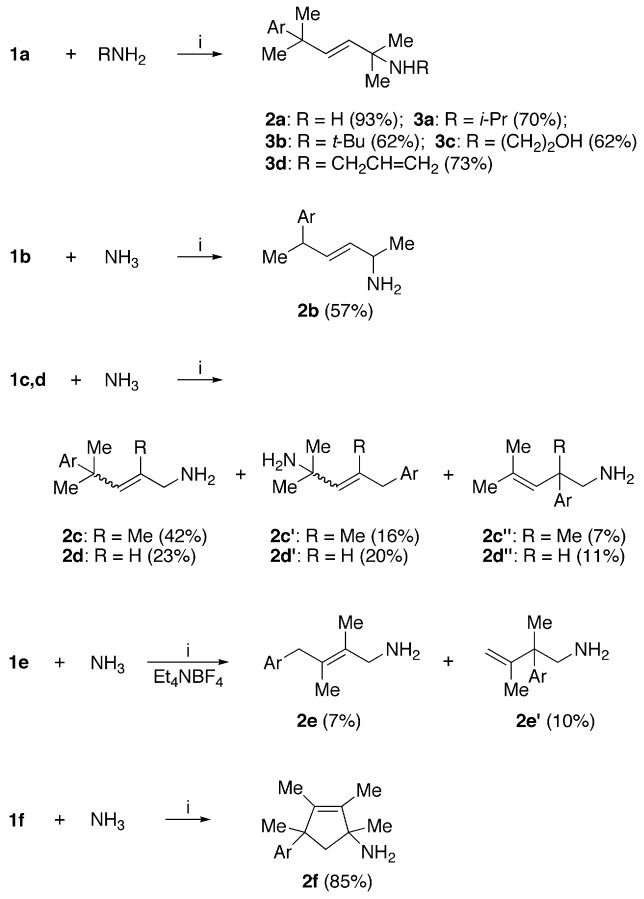
Table 1. Redox-photosensitized amination of alkadienes and alkenes (**1a–j**)[a]

Entry	1	RNH_2	*t* (h)[b]	Products (yields, %)[c]	Recovery (%)	
					DCB	S
1	**1a**	NH_3	8	**2a** (79)	8	94
2[d]	**1a**	NH_3	8	**2a** (93)	0	44
3[e]	**1a**	NH_3	8	**2a** (33)	55	—
4[f]	**1a**	NH_3	8	**2a** (0)	—	99
5	**1a**	*i*-$PrNH_2$	8	**3a** (70)	12	98
6[e]	**1a**	*i*-$PrNH_2$	8	**3a** (5)	87	—
7	**1a**	*t*-$BuNH_2$	8	**3b** (62)	16	99
8	**1a**	$HO(CH_2)_2NH_2$	8	**3c** (62)	5	99
9	**1a**	$CH_2{=}CHCH_2NH_2$	8	**3d** (73)	6	99
10	**1b**	NH_3	8	**2b** (57)	9	94
11[e]	**1b**	NH_3	24	**2b** (16)	47	—
12[f]	**1b**	NH_3	24	**2b** (0)	—	99
13	**1c**	NH_3	8	**2c** (42), **2c′** (16), **2c″** (7)	17	99
14	**1d**	NH_3	8	**2d** (23), **2d′** (20), **2d″** (11)	43	73
15[g]	**1e**	NH_3	8	**2e** (7), **2e′** (10)	67	82
16	**1f**	NH_3	8	**2f** (85)[h]	9	91
17	**1g**	NH_3	8	**2g** (42), **4a** (22)	14	94
18[g]	**1g**	NH_3	8	**2g** (39), **4a** (12)	30	87
19[d]	**1g**	NH_3	8	**2g** (31), **4a** (17)	34	50
20[g]	**1g**	*i*-$PrNH_2$	8	**3e** (20), **2g** (23), **5** (18), **6** (8)	34	78
21[g]	**1h**	NH_3	20	**2h** (17), **4b** (trace)	74	95
22	**1i**	NH_3	10	**2i** (43)[i]	27	100
23	**1j**	NH_3	20	**2j** (24)	33	74

[a] Irradiation of an ammonia-saturated MeCN–H_2O solution (19:1, 70 mL) containing **1** (7 mmol), DCB (3.5 mmol), and sensitizer (1 mmol).
[b] Irradiation time.
[c] Isolated yields based on DCB used.
[d] Using BN (1 mmol) as a sensitizer instead of TPB.
[e] In the absence of TPB.
[f] In the absence of DCB.
[g] In the presence of Et_4NBF_4 (0.1 mol dm^{-3}).
[h] cis and trans isomers ratio was 1:0.35.
[i] cis and trans isomers ratio was 1:1.18.

(Table 1, entry 1). A similar type of product was formed by the photoreaction of **1a** with MeOH in the presence of biphenyl and DCB pair.[8b] Also, the BN-photosensitized amination of **1a** gave **2a** in a high yield (93%) (entry 2). The photoamination of **1a** without the sensitizer, however, was inefficient (33%, entry 3). It was confirmed that the TPB-photosensitization in the absence of DCB gave no aminated product (entry 4). Scheme 3 summarizes the aminated products with the optimal yields.

The TPB-photosensitized amination of 2,4-hexadiene (**1b**) with NH_3 gave a diastereomeric mixture of 4-(4-amino-1-methyl-2-pentenyl)benzonitrile (**2b**) in a 57% yield (entry 10). The regioselectivity was examined for the photoamination of unsymmetrical 2,4-dimethyl-1,3-pentadiene (**1c**) and 4-methyl-1,3-pentadiene (**1d**) with NH_3. These photoaminations gave both 1,4-adducts (**2c**,**d** and **2c′**,**d′**) and a 1,2-adduct (**2c″** and **2d″**) (entries 13 and 14). In the case of the photoamination of 2,3-dimethyl-1,3-butadiene (**1e**) whose $E^{ox}_{1/2}$ (1.64 V) was higher than that of TPB, no aminated



Scheme 3. Reagents: (i) *hν*, TPB, DCB, MeCN–H_2O (19:1); Ar–=*p*-NC–C_6H_4–.

product was obtained. The photoamination gave **2e**,**e′** in low yields in the presence of Et_4NBF_4 (0.1 mol dm^{-3}), which was well known to enhance the efficiency of the electron transfer (entry 15).[10,11] The stereoselectivity was examined for the photoamination of cyclopentadiene derivative (**1f**), which gave an 85% yield of cis and trans isomers of 4-(4-amino-1,2,3,4-tetramethyl-2-cyclopentenyl)benzonitrile (**2f**) in a ratio of 1:0.35 (entry 16). The stereochemistry of *cis*-**2f** was confirmed by X-ray crystallographic analysis of the acetamide of *cis*-**2f** (Fig. 1).

The TPB-photosensitized amination was applied to simple alkenes. In the case of 2,3-dimethyl-2-butene (**1g**), the

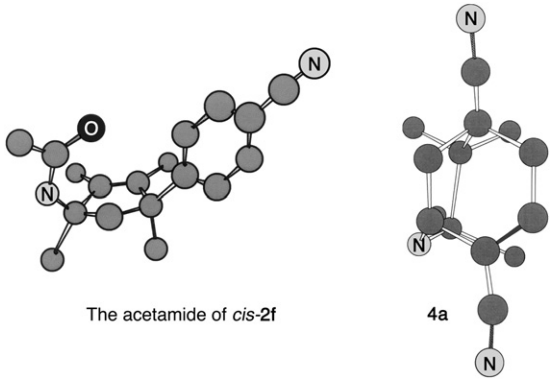
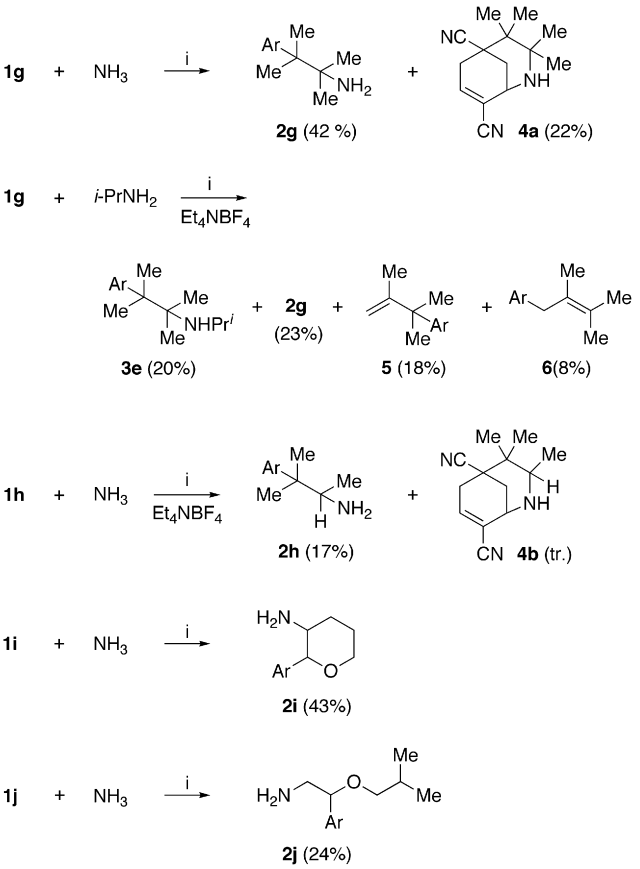


Figure 1. Crystal structure of the acetamide of *cis*-**2f** and **4a**.

typical photo-NOCAS adduct (**2g**) and unexpected azabicyclo compound (**4a**) were formed in 42 and 22% yields, respectively (Scheme 4, entry 17). The structure of **4a** was determined by X-ray crystallographic analysis (Fig. 1). Arnold has reported that the photo-NOCAS reaction of **1g** with MeOH gave 4-(2-methoxy-1,1,2-trimethylpropyl)-benzonitrile in a 70% yield as a sole product.[8b] The photoamination of 2-methyl-2-butene (**1h**) in the presence of Et_4NBF_4 gave 4-(2-amino-1,1-dimethylpropyl)benzonitrile (**2h**) and azabicyclo compound (**4b**) in low yields (entry 21). In the cases of 3,4-dihydro-2*H*-pyran (**1i**), cis and trans isomers of 4-(3-amino-tetrahydro-2-pyranyl)benzonitrile (**2i**) were obtained in a ratio of 1:1.18 (entry 22). 4-(2-Amino-1-isobutoxyethyl)benzonitrile (**2j**) was obtained from the photoamination of isobutyl vinyl ether (**1j**) (entry 23). In both adducts, the amino group was incorporated on the β-carbon of the double bond of these substrates, whereas no adduct incorporating the amino group on the α-carbon was obtained.



Scheme 4. Reagents: (i) *hν*, TPB, DCB, MeCN–H_2O (19:1); Ar–=*p*-NC–C_6H_4–.

Also the photoaminations of **1a** and **1g** with alkylamines were carried out by the TPB-photosensitization. Irradiation was performed for a degassed MeCN–H_2O (v/v, 19:1, 70 mL) containing **1** (7 mmol), DCB (3.5 mmol), TPB (1 mmol), and the amines (70 mmol). The TPB-photosensitized amination of **1a** with isopropylamine, *tert*-butylamine, ethanolamine, and allylamine gave the corresponding *N*-alkyl substituted **2a** (**3a–d**) in relatively good yields (entries 5, 7–9). The TPB-photosensitized amination was much more effective than the photoamination without TPB (entry 6). In the case of photoamination with ethanolamine, no product

was derived by the attack from the oxygen site of ethanolamine to **1a**, although MeOH acted as a nucleophile in photo-NOCAS reaction of **1a**.[8] The photoamination of **1g** with isopropylamine gave considerable amounts of **5** and **6** along with the formation of aminated products (**3e** and **2g**) (entry 20).

2.2. Mechanism

It was confirmed that TPB and BN played as redox-photosensitizers in the above photoamination, since the photoamination in the absence of DCB gave no aminated products and almost incident light was absorbed by the sensitizer under these reaction conditions. The value of free energy changes (ΔG) for the electron transfer from TPB or BN to DCB was calculated to be negative (-40 kJ mol^{-1} and -7 kJ mol^{-1}) by the Rehm–Weller equation,[12] as previously reported.[10] Therefore, an initiation step of this photoamination should be the electron transfer from the excited singlet states of the sensitizer to DCB, resulting in the cation radicals of the sensitizer and the anion radical of DCB ($DCB^{-\bullet}$). The hole transfer from the cation radicals of the sensitizer to **1** should be an important step for the efficient photoamination. The efficient photoamination requires that $E^{ox}_{1/2}$ of **1** is lower than that of TPB. In fact, the TPB-photosensitized amination of **1e** and **1h** whose $E^{ox}_{1/2}$ was near those of TPB gave the aminated products in low yields. The resulting $\mathbf{1}^{+\bullet}$ allowed the nucleophilic addition of RNH_2 followed by the radical coupling of the aminated radicals (**7**) with $DCB^{-\bullet}$ to give **2** according to Scheme 1.

Moreover, we elucidated that the reaction efficiency and regiochemistry depend on both the distribution of positive charge in $\mathbf{1}^{+\bullet}$ and the stability of **7** as previously reported.[4,7,10] Chart 1 shows the positive charge distribution in $\mathbf{1}^{+\bullet}$ calculated by ab initio method. When little positive charge was distributed over the reaction site in the case of **1i** and **1j**, the photoaminations were inefficient.

Azabicyclo compounds **4** would be obtained via the aminated anion (**8**) in competition with the elimination of CN^- from **8** to give **2**, as shown in Scheme 1. The photoamination of **1g** with *i*-$PrNH_2$ gave not only aminated products (**3e** and **2g**) but also **5** and **6**. Probably, in competition with the addition of *i*-$PrNH_2$ to $\mathbf{1g}^{+\bullet}$, the deprotonation from $\mathbf{1g}^{+\bullet}$ occurred to give the radical intermediate, which underwent radical coupling with $DCB^{-\bullet}$ and then followed by the elimination of CN^- to give **5** and **6**. However, it is possible that the formation of **5** and **6** proceeds by the radical coupling process proposed by Arnold in the photoreaction of **1g** with DCB in MeCN.[13]

3. Conclusions

The photoaminations of simple alkenes and alkadienes (**1**), which had no absorption at >300 nm could be accomplished using the redox-photosensitization. Efficient photoaminations were achieved in the following cases: the oxidation potentials of **1** were sufficiently lower than that of the sensitizer and the sufficient positive charge distributes over the reaction site of $\mathbf{1}^{+\bullet}$. On the contrary, the photoaminations are inefficient in the case of **1e** and **1h** whose $E^{ox}_{1/2}$ was relatively higher and in the case of **1i** and **1j** little positive charge was distributed over the reaction site. Moreover, the aminated products of simple alkenes and alkadienes were entirely photo-NOCAS type products, because their aminated radicals (**7**) have no stabilizing groups.

4. Experimental

4.1. General

Melting points were measured using open capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 250 and 62.9 MHz, respectively. Chemical shifts were reported in parts per million relative to TMS as an internal standard. Mass spectra were operated at an ionization voltage of 70 eV. GLC analysis was performed using a 25 m fused-silica capillary column. The ab initio calculation was performed on a Silicon graphics O2 workstation using the SPARTAN program.

MeCN was distilled from CaH_2. The amines were used as received. Commercially available **1** was distilled from sodium under reduced pressure before use, and TPB[14] and BN[15] were prepared according to literature method.

4.2. General procedure of photoamination

An ammonia-saturated MeCN–H_2O solution (v/v, 19:1, 70 mL) of **1a–j** (7 mmol), DCB (3.5 mmol), and sensitizer (1 mmol) was poured into a Pyrex glass tube, sealed with a rubber septum, and irradiated with a high-pressure mercury lamp for 8–24 h at ambient temperature. In the cases of photoamination with RNH_2, a MeCN–H_2O (v/v, 19:1, 70 mL) solution containing **1** (7 mmol), DCB (3.5 mmol), and TPB (1 mmol) was bubbled with argon gas and then RNH_2 (70 mmol) was added and irradiated for 8 h. In the photoamination in the presence of Et_4NBF_4, 7 mmol of Et_4NBF_4 was added to the solutions (70 mL).

After irradiation, the photolysates were treated with Ac_2O to protect the amino group of the aminated products, and then sensitizer, DCB, and the acetamide of aminated products were isolated by chromatography on silica gel. The structural determination of the acetamide was performed on the basis of their spectroscopic and physical properties. In the case of photoaminations of **1a** with RNH_2 (entries 5–9), the photolysates were separated by chromatography on silica gel without the treatment of Ac_2O, because acetylation of **3a–d** was unsuccessful. In particular, **3b** was easily decomposed at room temperature, therefore the peaks of molecular ion of **3b–d** were not obtained in their mass spectra. In the case of **5** and **6**, the structural determination was performed by comparisons of the data with those published in the literature.[16]

4.2.1. (*E*)-4-(4-Amino-1,1,4-trimethyl-2-pentenyl)benzonitrile (2a). The acetamide; a white solid; mp 135.5–136.0 °C (from benzene–ethyl acetate); ^1H NMR δ 1.39 (s, 6H), 1.43 (s, 6H), 1.93 (s, 3H), 5.62 (br s, 1H), 5.63 (d, J=16.0 Hz, 1H), 5.73 (d, J=15.9 Hz, 1H), 7.46–7.48 (m, 2H), 7.56–7.60 (m, 2H); ^{13}C NMR δ 24.35, 27.73, 28.58, 40.60, 53.75, 109.54, 119.15, 127.17, 131.98, 133.67,

135.49, 154.86, 169.13; IR ($CHCl_3$, cm^{-1}): 3442, 2972, 2229, 1675, 1505. HRMS calcd for $C_{17}H_{22}N_2O$: 270.1732; found: 270.1680. Calcd for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36%. Found C, 75.43; H, 8.08; N, 10.29%.

4.2.2. (*E*)-4-(4-Amino-1-methyl-2-pentenyl)benzonitrile (2b). A yellow oil; IR (neat, cm^{-1}): 3287, 2972, 2228. The acetamide; a yellow oil; ^1H NMR δ 1.22 (t, J=6.8 Hz, 3H), 1.35 (d, J=7.0 Hz, 3H), 1.96 (s, 3H), 3.45–3.55 (m, 1H), 4.50–4.60 (m, 1H), 5.47 (ddd, J=15.5, 5.4, 1.2 Hz, 1H), 5.63 (br s, 1H), 5.71 (ddd, J=15.5, 6.5, 1.3 Hz, 1H), 7.30 (d, J=8.4 Hz, 2H), 7.58 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 20.65, 20.70, 20.92, 23.24, 41.69, 46.18, 109.76, 119.00, 128.13, 131.73, 132.24, 133.16, 151.37, 169.41. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1417; found: 242.1408.

4.2.3. 4-(4-Amino-1,1,3-trimethyl-2-butenyl)benzonitrile (2c). The acetamide of *E*-isomer; a colorless oil; ^1H NMR δ 1.13 (d, J=1.1 Hz, 3H), 1.42 (s, 6H), 2.02 (s, 3H), 3.57 (d, J=5.9 Hz, 2H), 5.61 (d, J=1.3 Hz, 1H), 6.11 (br s, 1H), 7.46 (d, J=8.6 Hz, 2H), 7.57 (d, J=8.6 Hz, 2H); ^{13}C NMR δ 15.80, 23.22, 31.00, 39.87, 47.53, 109.13, 119.13, 127.04, 132.04, 133.83, 135.35, 156.18, 170.17; IR (neat, cm^{-1}): 3448, 3019, 2229, 1667. HRMS calcd for $C_{16}H_{20}N_2O$: 256.1575; found: 256.1566. The acetamide of *Z*-isomer; a colorless oil; ^1H NMR δ 1.14 (d, J=1.2 Hz, 3H), 1.44 (s, 3H), 1.45 (s, 3H), 1.93 (s, 3H), 3.40–3.57 (m, 2H), 5.47 (d, J=1.2 Hz, 1H), 5.55 (br t, 1H), 7.48 (d, J=8.3 Hz, 2H), 7.61 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 19.86, 23.31, 24.97, 26.70, 44.43, 50.61, 109.85, 118.90, 127.78, 129.44, 132.15, 136.25, 152.68, 170.24. HRMS calcd for $C_{16}H_{20}N_2O$: 256.1575; found: 256.1564.

4.2.4. 4-(4-Amino-2,4-dimethyl-2-pentenyl)benzonitrile (2c′). The product was obtained as a mixture of *E* and *Z* isomers. The acetamide of *E*-isomer; a colorless oil; ^1H NMR δ 1.50 (s, 6H), 1.57 (d, J=1.2 Hz, 3H), 1.80 (s, 3H), 3.65 (s, 2H), 5.65 (br s, 1H), 5.86 (br s, 1H), 7.30 (d, J=8.1 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H); ^{13}C NMR δ 23.96, 24.16, 28.69, 38.04, 52.89, 109.83, 119.02, 129.42, 132.13, 132.23, 134.76, 145.35, 168.92; the acetamide of *Z*-isomer; ^1H NMR δ 1.48 (s, 6H), 1.61 (d, J=1.2 Hz, 3H), 1.93 (s, 3H), 3.32 (s, 2H), 5.54 (br s, 1H), 5.79 (br s, 1H), 7.30 (d, J=8.1 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H); ^{13}C NMR δ 16.54, 23.86, 28.53, 47.35, 52.89, 109.83, 119.20, 129.63, 132.13, 132.99, 134.57, 145.97, 168.70. HRMS calcd for $C_{16}H_{20}N_2O$: 256.1575; found: 256.1575.

4.2.5. 4-(1-Aminomethyl-1,3-dimethyl-2-butenyl)benzonitrile (2c″). The acetamide; a colorless oil; ^1H NMR δ 1.70 (s, 3H), 1.75 (s, 6H), 1.85 (s, 3H), 3.33 (d, J=5.3 Hz, 2H), 5.20 (br s, 1H), 5.72 (br s, 1H), 7.48 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H); ^{13}C NMR δ 22.11, 23.02, 28.69, 31.62, 40.04, 40.37, 109.47, 118.90, 127.03, 129.63, 133.52, 138.14, 156.66, 169.86. HRMS calcd for $C_{16}H_{20}N_2O$: 256.1575; found: 256.1525.

4.2.6. 4-(4-Amino-1,1-dimethyl-2-butenyl)benzonitrile (2d). The acetamide; a yellow oil; ^1H NMR δ 1.40 (s, 6H), 2.00 (s, 3H), 3.89 (dt, J=5.9, 1.2 Hz, 2H), 5.49 (dt, J=15.6, 5.6 Hz, 1H), 5.70 (br s, 1H), 5.75 (dt, J=15.6, 1.2 Hz, 1H), 7.42 (d, J=8.4 Hz, 2H), 7.58 (d, J=8.6 Hz, 2H); ^{13}C NMR δ 23.24, 28.33, 40.76, 41.36, 109.73, 118.94, 123.69, 126.96, 131.99, 140.98, 153.99, 169.80. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1373.

4.2.7. 4-(4-Amino-4-methyl-2-pentenyl)benzonitrile (2d′). The acetamide; a yellow oil; ^1H NMR δ 1.42 (s, 6H), 1.93 (s, 3H), 3.42 (d, J=6.6 Hz, 2H), 5.46 (br s, 1H), 5.60 (dt, J=15.6, 6.7 Hz, 1H), 5.81 (dt, J=15.6, 1.3 Hz, 1H), 7.30 (d, J=8.3 Hz, 2H), 7.57 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 27.55, 38.54, 53.77, 109.90, 119.00, 124.46, 129.29, 132.18, 138.67, 146.17, 169.15. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1468.

4.2.8. 4-(1-Aminomethyl-3-methyl-2-butenyl)benzonitrile (2d″). The acetamide; a yellow oil; ^1H NMR δ 1.66 (d, J=1.1 Hz, 3H), 1.75 (d, J=1.0 Hz, 3H), 1.93 (s, 3H), 3.30–3.42 (m, 1H), 3.49–3.60 (m, 1H), 3.77–3.87 (m, 1H), 5.20–5.27 (m, 1H), 5.58 (br s, 1H), 7.34 (d, J=8.2 Hz, 2H), 7.60 (d, J=8.4 Hz, 2H); ^{13}C NMR δ 18.24, 23.14, 25.82, 44.18, 44.65, 110.23, 118.78, 123.69, 128.35, 132.34, 136.15, 148.43, 170.07. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1376.

4.2.9. (*E*)-4-(4-Amino-2,3-dimethyl-2-butenyl)benzonitrile (2e). The acetamide; a yellow oil; ^1H NMR δ 1.61 (d, J=0.8 Hz, 3H), 1.77 (d, J=0.8 Hz, 3H), 1.98 (s, 3H), 3.55 (s, 2H), 3.95 (d, J=5.5 Hz, 2H), 5.56 (br s, 1H), 7.25 (d, J=8.3 Hz, 2H), 7.58 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 17.37, 19.00, 23.30, 40.00, 48.33, 110.62, 119.11, 128.02, 129.27, 130.38, 132.32, 146.12, 170.12. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1376.

4.2.10. 4-(1-Aminomethyl-1,2-dimethylallyl)benzonitrile (2e′). The acetamide; a yellow oil; ^1H NMR δ 1.40 (s, 3H), 1.52 (d, J=0.9 Hz, 3H), 1.97 (s, 3H), 3.64 (dd, J=13.2, 5.0 Hz, 1H), 3.78 (dd, J=13.2, 6.5 Hz, 1H), 5.06 (s, 1H), 5.16–5.17 (m, 1H), 5.33 (br s, 1H), 7.40 (d, J=8.4 Hz, 2H), 7.64 (d, J=8.4 Hz, 2H); ^{13}C NMR δ 20.19, 23.46, 23.90, 42.52, 45.78, 110.62, 113.82, 118.80, 127.45, 132.42, 147.68, 150.47, 170.33. HRMS calcd for $C_{15}H_{18}N_2O$: 242.1419; found: 242.1376.

4.2.11. 4-(4-Amino-1,2,3,4-tetramethyl-2-cyclopentenyl)-benzonitrile (2f). The acetamide of cis-isomer; a white solid; mp 141.5–142.0 °C (from benzene); ^1H NMR δ 1.35 (s, 3H), 1.42 (s, 3H), 1.47 (s, 3H), 1.63 (s, 3H), 1.90 (s, 3H), 2.02 (d, J=13.5 Hz, 1H), 2.67 (d, J=13.5 Hz, 1H), 6.03 (s, 1H), 7.57 (d, J=8.5 Hz, 2H), 7.63 (d, J=8.5 Hz, 2H); ^{13}C NMR δ 9.79, 10.86, 23.79, 24.29, 26.86, 52.76, 54.32, 65.90, 108.99, 119.36, 127.93, 131.79, 135.84, 138.29, 155.22, 169.63; IR ($CHCl_3$, cm^{-1}): 3442, 2973, 2227, 1673, 1506. HRMS calcd for $C_{18}H_{22}N_2O$: 282.1731; found: 282.1765. The acetamide of trans-isomer; a yellow oil; ^1H NMR δ 1.30 (s, 3H), 1.47 (s, 3H), 1.52 (s, 3H), 1.69 (s, 3H), 1.95 (s, 3H), 2.01 (d, J=13.8 Hz, 1H), 2.69 (d, J=13.7 Hz, 1H), 6.07 (s, 1H), 7.31 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H); ^{13}C NMR δ 9.79, 11.13, 23.99, 25.16, 25.53, 53.32, 54.04, 65.84, 109.22, 119.10, 127.26, 132.04, 136.39, 138.41, 155.22, 169.75; IR ($CHCl_3$, cm^{-1}): 3449, 3019, 2229, 1667, 1517. HRMS calcd for $C_{18}H_{22}N_2O$: 282.1731; found: 282.1740.

4.2.12. 4-(2-Amino-1,1,2-trimethylpropyl)benzonitrile (2g). The acetamide; a white solid; mp 133.0–133.5 °C

(from MeOH). ^{1}H NMR δ 1.34 (s, 6H), 1.46 (s, 6H), 1.90 (s, 3H), 4.94 (br s, 1H), 7.53 (d, J=8.6 Hz, 2H), 7.62 (d, J=8.6 Hz, 2H), ^{13}C NMR δ 24.13, 24.58, 25.04, 46.39, 59.30, 110.19, 116.71, 128.84, 131.27, 151.63, 169.30; IR ($CHCl_3$, cm^{-1}): 3434, 2994, 2230, 1677, 1515. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47%. Found C, 73.27; H, 8.06; N, 11.41%.

4.2.13. 4-(2-Amino-1,1-dimethylpropyl)benzonitrile (2h). The acetamide; a yellow oil; ^{1}H NMR δ 0.90 (d, J=6.8 Hz, 3H), 1.32 (s, 3H), 1.33 (s, 3H), 1.94 (s, 3H), 4.39 (dq, J=9.8, 3.4 Hz, 1H), 5.16 (d, J=10.4 Hz, 1H), 7.49 (d, J=8.6 Hz, 2H), 7.62 (d, J=8.5 Hz, 2H), ^{13}C NMR δ 16.79, 23.38, 23.65, 25.97, 42.65, 52.39, 110.34, 118.70, 127.41, 132.16, 152.50, 169.56. HRMS calcd for $C_{14}H_{18}N_2O$: 230.1419; found: 230.1403.

4.2.14. 4-(3-Amino-tetrahydro-2-pyranyl)benzonitrile (2i). The acetamide of trans-isomer; a white solid; mp 208.0–209.0 °C (from benzene–ethyl acetate); ^{1}H NMR δ 1.51–1.69 (m, 1H), 1.76 (s, 3H), 1.80–2.01 (m, 2H), 2.12–2.18 (m, 1H), 3.53 (dt, J=3.0, 11.5 Hz, 1H), 3.91–4.12 (m, 2H), 4.12 (d, J=9.8 Hz, 1H), 5.69 (d, J=9.3 Hz, 1H), 7.49 (d, J=8.3 Hz, 2H), 7.61 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 23.16, 25.58, 30.87, 50.61, 68.25, 83.13, 111.79, 118.82, 128.17, 131.95, 144.89, 169.06; IR ($CHCl_3$, cm^{-1}): 3435, 3011, 2230, 1672, 1512. HRMS calcd for $C_{14}H_{16}N_2O_2$: 244.1212; found: 244.1206. The acetamide of cis-isomer; a colorless oil; ^{1}H NMR δ 1.53–1.65 (m, 1H), 1.78 (s, 3H), 1.81–2.09 (m, 3H), 3.63–3.74 (m, 1H), 4.16–4.28 (m, 1H), 4.42–4.54 (m, 1H), 4.63 (s, 1H), 6.06 (d, J=9.0 Hz, 1H), 7.44 (d, J=8.3 Hz, 2H), 7.61 (d, J=8.3 Hz, 2H); ^{13}C NMR δ 20.56, 22.99, 28.66, 47.15, 69.09, 79.46, 111.00, 118.84, 126.16, 131.92, 144.98, 169.49; MS m/z 244 (M^+).

4.2.15. 4-(2-Amino-1-isobutoxyethyl)benzonitrile (2j). The acetamide; a yellow oil; ^{1}H NMR δ 0.91 (d, J=6.7 Hz, 3H), 0.92 (d, J=6.6 Hz, 3H), 1.86–1.99 (m, 1H), 2.00 (s, 3H), 3.11 (d, J=6.5 Hz, 2H), 3.14–3.25 (m, 1H), 3.60–3.70 (m, 1H), 4.44 (dd, J=8.4, 3.9 Hz, 1H), 6.32 (br t, 1H), 7.46 (d, J=8.3 Hz, 2H), 7.66 (d, J=8.2 Hz, 2H); ^{13}C NMR δ 19.03, 19.13, 22.92, 28.33, 45.31, 76.16, 79.87, 111.39, 118.47, 127.12, 132.12, 145.42, 120.08. HRMS calcd for $C_{15}H_{20}N_2O_2$: 260.1525; found: 260.1540.

4.2.16. (*E*)-4-(4-Isopropylamino-1,1,4-trimethyl-2-pentenyl)benzonitrile (3a). A yellow oil; ^{1}H NMR δ 1.03 (d, J=6.4 Hz, 6H), 1.19 (s, 6H), 1.41 (s, 6H), 1.45 (br s, 1H), 2.82 (sept, J=6.4 Hz, 1H), 5.45 (d, J=16.1 Hz, 1H), 5.58 (d, J=16.1 Hz, 1H), 7.41–7.45 (m, 2H), 7.56–7.60 (m, 2H); ^{13}C NMR δ 26.00, 28.34, 28.69, 40.6, 43.50, 54.18, 109.63, 119.03, 127.03, 131.95, 135.48, 136.62, 154.86; IR (neat, cm^{-1}): 2967, 2227. HRMS calcd for $C_{18}H_{26}N_2$: 270.2096; found: 270.2141.

4.2.17. (*E*)-4-(4-*tert*-Butylamino-1,1,4-trimethyl-2-pentenyl)benzonitrile (3b). A colorless oil; ^{1}H NMR δ 1.16 (s, 9H), 1.29 (s, 6H), 1.41 (s, 6H), 5.51 (d, J=16.2 Hz, 1H), 5.67 (d, J=16.2 Hz, 1H), 7.41–7.44 (m, 2H), 7.56–7.59 (m, 2H); IR (neat, cm^{-1}): 2971, 2229; ^{13}C NMR δ 28.31, 30.90, 32.42, 40.43, 52.61, 54.90, 109.55, 118.92, 126.95, 131.89, 133.42, 138.83, 154.87.

4.2.18. (*E*)-4-[4-(2-Hydroxy-ethylamino)-1,1,4-trimethyl-2-pentenyl]benzonitrile (3c). A white solid; mp 76.5–78.0 °C (from benzene); ^{1}H NMR δ 1.21 (s, 6H), 1.41 (s, 6H), 2.61–2.66 (m, 2H), 2.99 (br s, 2H), 3.62–3.66 (m, 2H), 5.45 (d, J=16.1 Hz, 1H), 5.64 (d, J=16.1 Hz, 1H), 7.42–7.46 (m, 2H), 7.57–7.60 (m, 2H); ^{13}C NMR δ 27.44, 28.68, 40.68, 44.55, 53.59, 61.53, 109.55, 119.02, 127.04, 131.97, 135.15, 136.66, 154.73; IR (neat, cm^{-1}): 2970, 2229.

4.2.19. (*E*)-4-(4-Allylamino-1,1,4-trimethyl-2-pentenyl)-benzonitrile (3d). A yellow oil; ^{1}H NMR δ 1.21 (s, 6H), 1.42 (s, 6H), 3.12 (d, J=6.1 Hz, 2H), 5.05 (dd, J=10.1, 1.6 Hz, 1H), 5.15 (dd, J=17.1, 1.6 Hz, 1H), 5.45 (d, J=16.1 Hz, 1H), 5.64 (d, J=16.1 Hz, 1H), 5.92 (ddt, J=17.1, 10.1, 6.1 Hz, 1H), 7.42–7.46 (m, 2H), 7.56–7.59 (m, 2H); ^{13}C NMR δ 27.57, 28.70, 40.65, 46.06, 53.74, 109.58, 115.38, 118.95, 127.06, 131.91, 135.38, 136.41, 137.50, 154.73; IR (neat, cm^{-1}): 2969, 2227.

4.2.20. 4-(2-Isopropylamino-1,1,2-trimethylpropyl)-benzonitrile (3e). A colorless oil; ^{1}H NMR δ 0.97 (d, J=6.3 Hz, 6H), 0.99 (s, 6H), 1.36 (s, 6H), 2.86 (sept, J=6.3 Hz, 1H), 3.23 (br s, 1H), 7.55 (d, J=8.6 Hz, 2H), 7.61 (d, J=8.6 Hz, 2H); ^{13}C NMR δ 22.69, 24.19, 26.29, 43.09, 45.85, 57.99, 109.22, 119.23, 129.63, 130.56, 153.18; IR (neat, cm^{-1}): 2973, 2226. HRMS (CI) calcd for $C_{16}H_{25}N_2$ (MH^+): 245.2018; found: 245.2013.

4.2.21. 3,3,4,4-Tetramethyl-2-azabicyclo[3.3.1]non-7-ene-5,8-dicarbonitrile (4a). A white solid; mp 176.5–178.5 °C (from MeOH); ^{1}H NMR δ 1.01 (s, 3H), 1.15 (s, 6H), 1.39 (s, 3H), 1.56 (br s, 1H), 1.86 (dd, J=12.7, 2.6 Hz, 1H); 2.54 (ddd, J=12.7, 3.6, 1.3 Hz, 1H), 2.86 (dd, J=21.0, 3.2 Hz, 1H), 3.12 (ddd, J=21.0, 4.3, 1.3 Hz, 1H), 3.62 (dd, J=3.6, 2.6 Hz, 1H), 6.58 (dd, J=4.3, 3.2 Hz, 1H); ^{13}C NMR δ 20.99, 24.53, 27.67, 31.04, 31.92, 34.25, 40.03, 40.24, 46.98, 54.84, 118.00, 118.50, 123.88, 143.63; IR ($CHCl_3$, cm^{-1}): 2989, 2235, 2218; MS m/z 229 (M^+).

4.2.22. 3,4,4-Trimethyl-2-azabicyclo[3.3.1]non-7-ene-5,8-dicarbonitrile (4b). The acetamide; a white solid; mp 165.0–167.0 °C (from benzene–ethyl acetate); ^{1}H NMR δ 1.10 (s, 3H), 1.24 (s, 3H), 1.53 (d, J=7.1 Hz, 3H), 1.94 (dd, J=13.3, 2.5 Hz, 1H), 2.23 (s, 3H), 2.46 (dd, J=13.4, 3.4 Hz, 1H), 2.75 (dd, J=20.7, 3.2 Hz, 1H), 2.94 (dd, J=20.7, 4.3 Hz, 1H), 3.40 (q, J=7.1 Hz, 1H), 1.92 (br t, 1H), 6.97 (dd, J=4.3, 3.2 Hz, 1H); ^{13}C NMR δ 15.00, 16.20, 23.12, 24.78, 31.35, 32.66, 39.86, 40.96, 49.51, 54.24, 110.86, 116.75, 121.77, 147.10, 170.80; IR ($CHCl_3$, cm^{-1}): 3022, 2238, 2223, 1668. HRMS calcd for $C_{15}H_{19}N_3O$: 257.1528; found: 257.1520.

4.3. The X-ray crystallographic analysis

X-ray crystallographic analysis of acetamide of *cis*-**2f** and **4a** was performed on an Enraf-Nonius CAD-4 system using Mo Kα irradiation (λ=0.71069 Å). The molecular structures were drawn using Chem3D based on X-ray crystallographic data, as shown in Figure 1.

4.3.1. The crystal data of the acetamide of *cis*-2f. M=82.39, monoclinic. $P21$, a=9.961(13) Å, b=11.350(4) Å,

c=14.871(14) Å, β=100.673(7)°, V=1652.31 Å^3, Z=4, D_m=1.14 g cm^{-3}, D_{calcd}=1.19 g cm^{-3}, Rw=0.038, R=0.044, unique reflection=1429.

4.3.2. The crystal data of 4a. M=229.32, monoclinic. $P1$, a=11.860(13) Å, b=7.832(4) Å, c=14.772(14) Å, β=109.27(7)°, V=1295.23 Å^3, Z=4, D_m=1.19 g cm^{-3}, D_{calcd}=1.17 g cm^{-3}, Rw=0.080, R=0.078, unique reflection=3060.

References and notes

1. (a) Mariano, P. S.; Stavinoha, J. L. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, NY, 1984; pp 145–257; (b) Lewis, F. D. *Photo-induced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, pp 1–69.
2. Yasuda, M.; Shiragami, T.; Matsumoto, J.; Yamashita, T.; Shima, K. *Organic Photochemistry and Photophysics*; Ramamurthy, V., Schanze, K., Eds.; CRC: New York, NY, 2006; pp 207–253.
3. Yasuda, M.; Yamashita, T.; Shima, K.; Pac, C. *J. Org. Chem.* **1987**, *54*, 753–759.
4. Yamashita, T.; Shiomori, K.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 366–374.
5. Yasuda, M.; Isami, T.; Kubo, J.; Mizutani, M.; Yamashita, T.; Shima, K. *J. Org. Chem.* **1992**, *57*, 1351–1354.
6. Yamashita, T.; Yasuda, M.; Isami, T.; Tanabe, K.; Shima, K. *Tetrahedron* **1994**, *50*, 9275–9286.
7. Kojima, R.; Yamashita, T.; Tanabe, K.; Shiragami, T.; Yasuda, M.; Shima, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 217–222.
8. (a) Arnold, D. R.; Mcmanus, K. A.; Du, X. *Can. J. Chem.* **1994**, *72*, 415–429; (b) Mcmanus, K. A.; Arnold, D. R. *Can. J. Chem.* **1994**, *72*, 2291–2304.
9. Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499–4508.
10. Yasuda, M.; Kojima, R.; Tsutsui, H.; Utsunomiya, D.; Ishii, K.; Jinnouchi, K.; Shiragami, T.; Yamashita, T. *J. Org. Chem.* **2003**, *68*, 7618–7624.
11. (a) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455–458; (b) Santamaria, J. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part B, pp 483–540; (c) Yasuda, M.; Matsuzaki, Y.; Shima, K. *Chem. Lett.* **1989**, 551–554; (d) Mizuno, K.; Ichinose, N.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 1855–1860; (e) Yamashita, T.; Tsurusako, T.; Nakamura, N.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 857–862; (f) Mizuno, K.; Ichinose, N.; Yoshimi, Y. *J. Photochem. Photobiol., C, Photochem. Rev.* **2000**, *1*, 167–193.
12. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.
13. Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785–1802.
14. Doss, R. C.; Solomon, P. W. *J. Org. Chem.* **1964**, *29*, 1567–1574.
15. Deussen, H.-D.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841–6852.
16. Arnold, D. R.; Wong, P. C.; Marouris, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609–2619.