Photoinduced Nucleophilic Addition of Ammonia and Alkylamines to Aryl-Substituted Alkenes in the Presence of *p*-Dicyanobenzene

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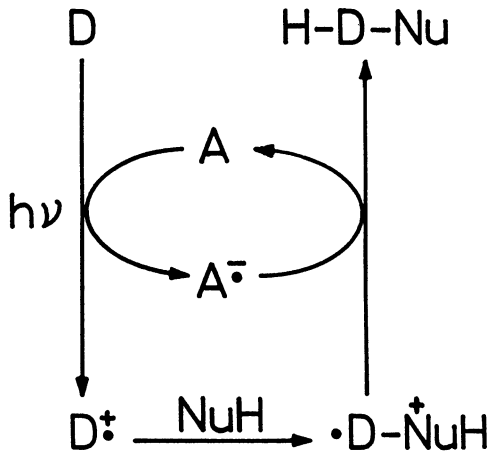
The photoamination of 1,1-diphenylpropene (**1a**) with ammonia and some primary alkylamines in the presence of *p*-dicyanobenzene gave the corresponding *N*-substituted 2-amino-1,1-diphenylpropane (**2a—e**) along with the formation of 3-methyl-4,4-diphenylbutanenitrile (**3a**), 1,1-diphenylpropane (**4a**), 3,3-diphenylpropene (**5**), and diphenylmethane (**6**). In the case of 1,1-diphenylethene (**1b**), *N*-substituted 1-amino-2,2-diphenylethane (**2f—h**), 4,4-diphenylbutanenitrile (**3b**), and 1,1-diphenylethane (**4b**) were produced. In photoamination with *t*-butylamine in acetonitrile, **3a** and **3b** were mainly formed as a consequence of the incorporation of acetonitrile to **1a** and **1b**. The photoamination of 1-phenyl-3,4-dihydronaphthalene (**1c**) with isopropylamine or *t*-butylamine gave *cis*- and *trans*-*N*-substituted 1-phenyl-2-amino-1,2,3,4-tetrahydronaphthalenes (**15** and **16**) in a ratio of ca. 8:2. The mechanism of photoamination is discussed in terms of a photochemical electron transfer of **1** to *p*-dicyanobenzene followed by a nucleophilic addition of the amine to the cation radical of **1**.

Photoinduced nucleophilic additions in the presence of electron acceptors have been investigated for a variety of electron-donating substances (D) involving aryl-substituted alkenes, strained compounds, and arenes from mechanistic and synthetic points of view.[1] In general, a key pathway for photoinduced nucleophilic additions is the addition of nucleophiles (NuH) to the cation radicals of D ($D^{+\cdot}$) generated from a photochemical electron transfer from D to electron acceptors (A), as shown in Scheme 1. While extensive studies on photoadditions using alcohols, water, and cyanide ion as nucleophiles have accumulated, little is known about the photoaddition of ammonia and amines, except for our reports on the photoamination of arenes with ammonia and alkylamines.[2] Since amines serve as both a nucleophile and a base, their photoaddition is expected to show different features from other nucleophiles. Herein we wish to report on the photoaddition of ammonia and alkylamines to aryl-substituted alkenes (**1**) using *p*-

Table 1. Photoamination of Diphenylalkene (**1**) with Ammonia and Alkylamines in the Presence of *p*-Dicyanobenzene[a]

Run	1	RNH_2	Products (Yield/%)[b]					Conv. of 1/%	Recov. of DCNB/%
1	**1a**	NH_3	**2a** (44)	**3a** (7)		**5** (5)	**6** (23)	76	78
2	**1a**	*i*-$PrNH_2$	**2b** (65)	**3a** (3)	**4a** (2)	**5** (8)	**6** (6)	81	92
			2a (21)						
3	**1a**	*t*-$BuNH_2$		**3a** (72)				100	83
4[c]	**1a**	*t*-$BuNH_2$	**2c** (46)		**4a** (2)	**5** (9)	**6** (12)	59	90
5	**1a**	$MeO(CH_2)_2NH_2$	**2d** (55)	**3a** (tr)	**4a** (4)	**5** (10)	**6** (7)	74	89
6	**1a**	$HO(CH_2)_2NH_2$	**2e** (58)	**3a** (7)	**4a** (1)	**5** (3)	**6** (2)	69	87
7[d]	**1b**	NH_3	**2f** (18)	**3b** (15)	**4b** (tr)	**7** (41)		70	96
8	**1b**	*i*-$PrNH_2$	**2g** (48)	**3b** (27)	**4b** (12)			28	100
			2f (8)						
9	**1b**	*t*-$BuNH_2$	**2h** (22)	**3b** (60)				66	98
10	**1b**	$MeO(CH_2)_2NH_2$	**2i** (19)	**3b** (6)	**4b** (3)	**8** (20)		80	93
11[e]	**1b**	*i*-$PrNH_2$		**3b** (7)	**4b** (17)	**9** (32)		84	—
12[f]	**1b**	*i*-$PrNH_2$			**4b** (12)	**10** (48)	**11** (13)	76	3
						12a(28)	**12b**(7)		
13[g]	**1b**	*i*-$PrNH_2$	**2g** (68)	**3b** (21)	**4b** (9)			22	94
14[h]	**1b**	*i*-$PrNH_2$	**2g** (36)	**3b** (15)	**4b** (19)			39	86

a) For deaerated acetonitrile solutions (150 ml) containing **1** (5.6 mmol), DCNB (16 mmol) and the amine (73 mmol). b) Isolated yields based on consumed **1**. c) For propanenitrile solution. d) For MeCN-H_2O (9:1) solution. e) In the absence of DCNB. f) For DMF solution. g) Redox-photosensitization by phenanthrene; after the photoreaction, 13% of phenanthrene was recovered. *N*-Isopropyl-9-amino-9,10-dihydrophenanthrene (**13**) was isolated in 44% yield based on phenanthrene used. h) Redox-photosensitization by triphenylene; 13% of triphenylene was recoverd after the photoreaction.

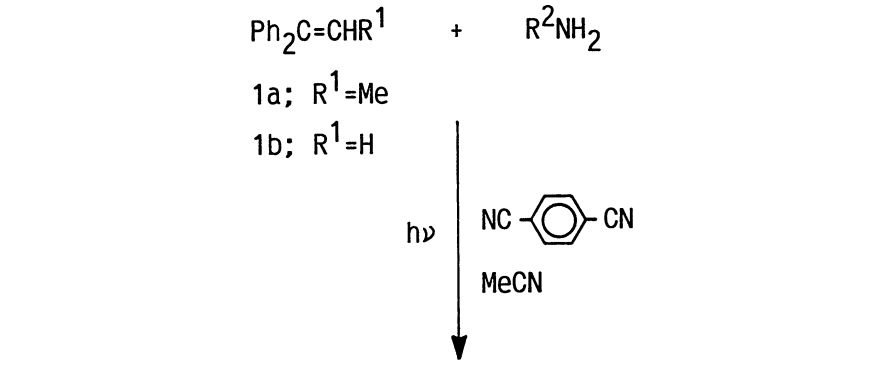


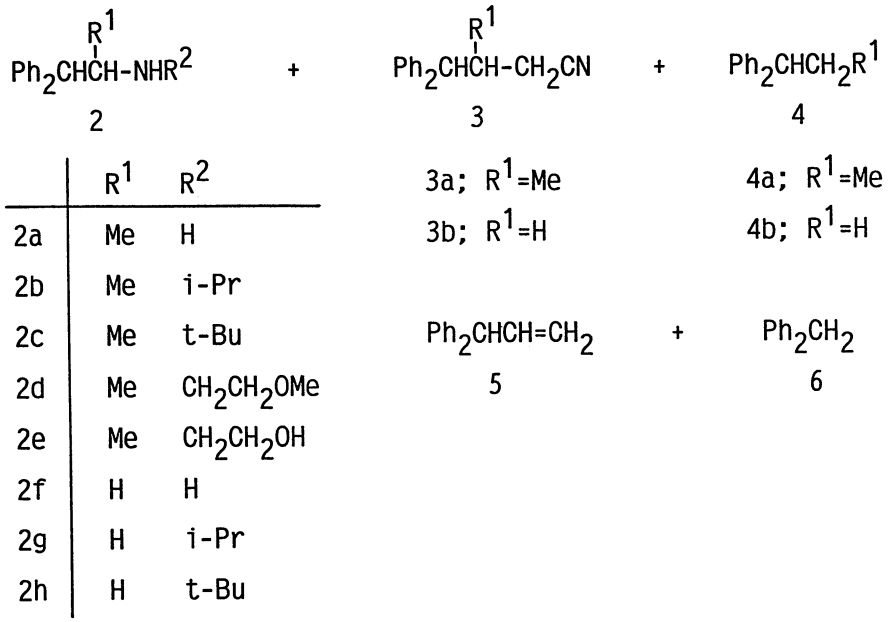
Scheme 1.

dicyanobenzene (DCNB) as A.

Results

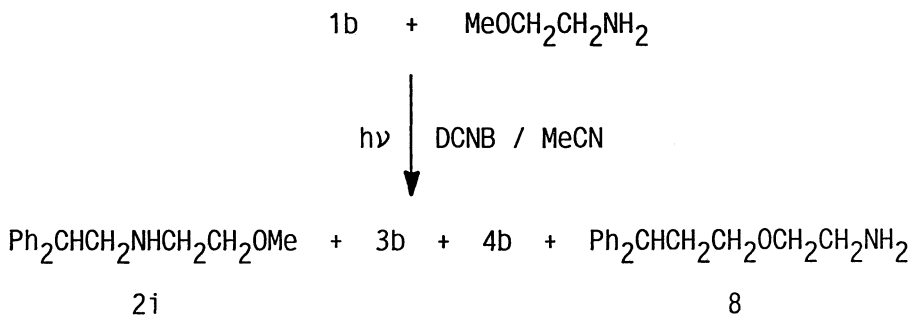
The photoamination of diphenylalkene (**1**) was carried out by irradiating a deaerated acetonitrile solution of **1**, DCNB, and ammonia or alkylamines through a Pyrex filter with a high-pressure mercury lamp; incident light was absorbed by both **1** and DCNB under these conditions. The results are summarized in Table 1 and Scheme 2. The photoamination of 1,1-diphenylpropene (**1a**) with ammonia, isopropylamine, 2-methoxyethylamine, and 2-aminoethanol gave the *N*-substituted 2-amino-1,1-diphenylpropanes (**2a—e**) accompanied by the formation of considerable amounts of 3-methyl-4,4-diphenylbutanenitrile (**3a**), 1,1-diphenylpropane (**4a**), 3,3-diphenylpropene (**5**), and diphenylmethane (**6**). Similarly, *N*-substituted 1-amino-2,2-diphenylethanes (**2f—h**), 4,4-diphenylbutanenitrile (**3b**), and 1,1-diphenylethane (**4b**) were formed from the photoamination of 1,1-diphenylethene (**1b**) with ammonia, isopropylamine, and *t*-butylamine. The photoamination of **1b** with 2-methoxyethylamine gave *N*-(2-methoxyethyl)-2,2-diphenylethylamine (**2i**) along with the formation of 1-(2-aminoethoxy)-3,3-diphenylpropane (**8**), **3b**, and **4b** (Scheme 3). In all cases, DCNB was mostly



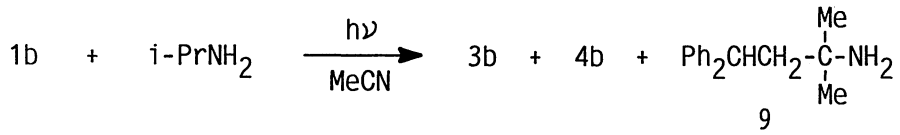


	R^1	R^2
2a	Me	H
2b	Me	i-Pr
2c	Me	t-Bu
2d	Me	CH_2CH_2OMe
2e	Me	CH_2CH_2OH
2f	H	H
2g	H	i-Pr
2h	H	t-Bu

Scheme 2.



Scheme 3.



Scheme 4.

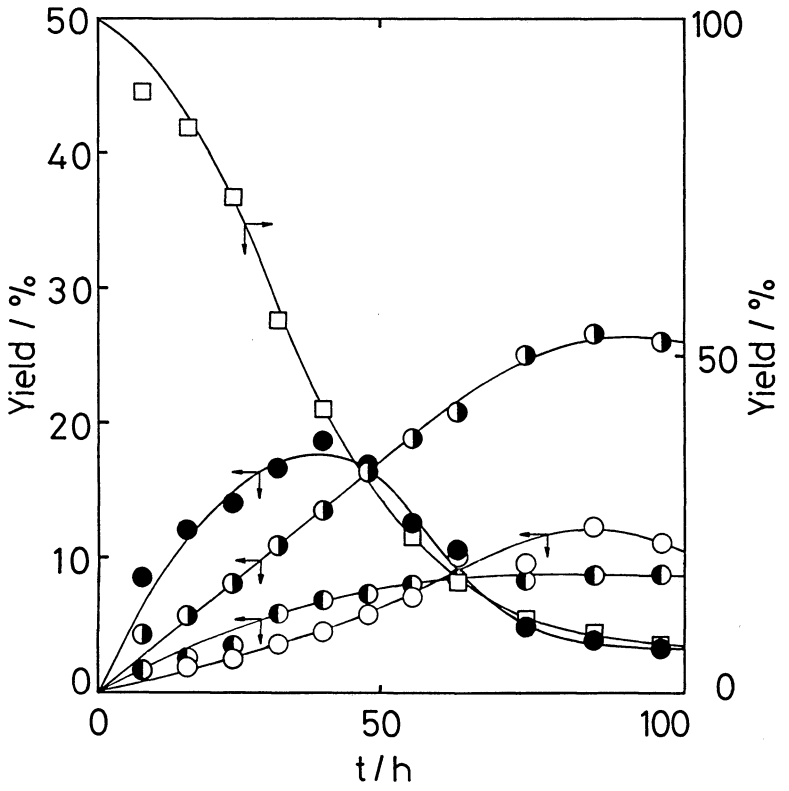


Fig. 1. Time-conversion plots for the disappearance of **1b** (—□—) and for the formation of **2f** (—○—), **2g** (—●—), **3b** (—◑—), and **4b** (—◐—) for the photoamination of **1b** with *i*-$PrNH_2$.

recovered after photoamination. It was confirmed that the photoamination which takes place to afford the aminated products (**2**) does not occur in the absence of an electron acceptor; e.g. the photoreaction of **1b** with isopropylamine in the absence of DCNB gave **3b**, **4b**, and 1,1-dimethyl-3,3-diphenylpropylamine (**9**) (Scheme 4).

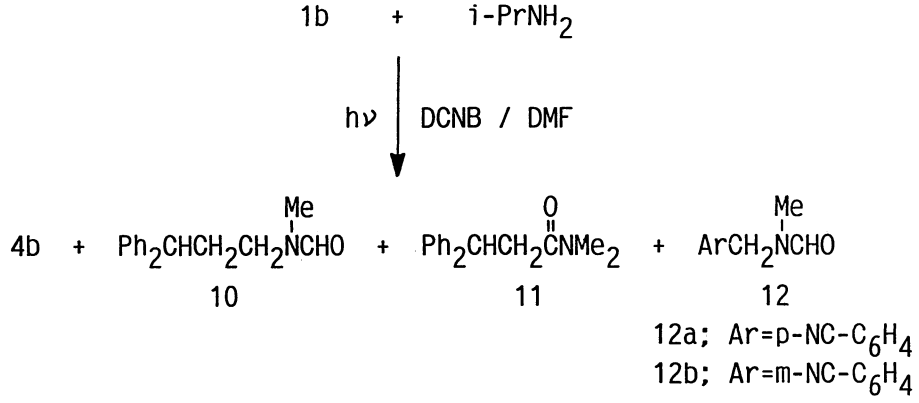
Photoamination with isopropylamine gave both **2a** and **2b** from **1a**, and **2f** and **2g** from **1b** in addition to other products. Figure 1 shows plots of the yields of **2f**, **2g**, **3b**, and **4b** vs. the irradiation time for the photoamination of **1b** with isopropylamine; the yields of **3b** and **4b** increased with an increase in the conversion of **1b**, whereas the yield of **2f** gradually increased

at the expense of **2g**.

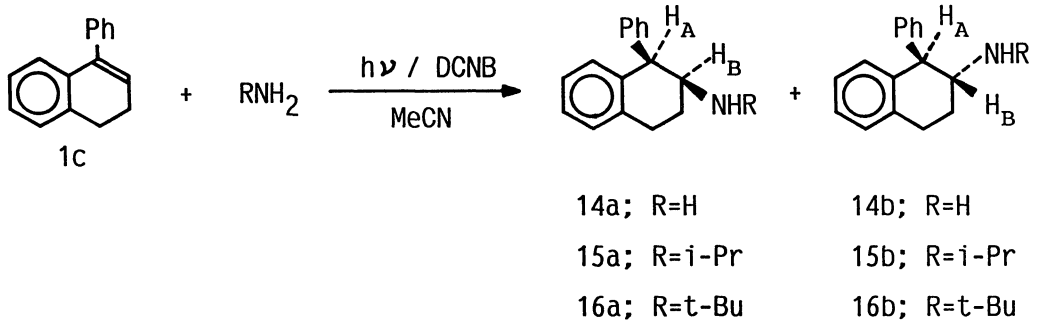
Although acetonitrile has been found to be an excellent solvent for the photoamination of arenes,[2] the photoamination of **1a** and **1b** in acetonitrile gave considerable amounts of acetonitrile-incorporated products (**3a,b**). It is noteworthy that the photoamination of **1a** and **1b** with *t*-butylamine gave **3a,b** as the major product. It was also found that the photoamination of **1a** with *t*-butylamine occurred in propanenitrile to give **2c** without photoreaction with the nitrile group of the solvent. No photoamination of **1b** occurred in *N,N*-dimethylformamide (DMF), 1,2-dimethoxyethane, or benzene; the photoreaction of **1b** in DMF gave adducts (**10**, **11**, and **12a,b**) of DMF with either **1b** or DCNB (Scheme 5).[3] In the photoamination of **1b** with ammonia in acetonitrile-water (9:1), 2,2-diphenylethanol (**7**) was produced in consequence to the photoaddition of water to **1b** along with the formation of **2f**.

Since electron-transfer photosensitization by 9,10-dicyanoanthracene (DCA)[4,5] and 1-naphthonitrile (CNN)[6] or redox-photosensitization[7] by aromatic hydrocarbons have provided useful tools for the photoaddition of alcohols to a variety of aryl-substituted alkenes, these methods were attempted in the present photoamination. However, no photoamination of **1b** with isopropylamine occurred by DCA- or CNN-photosensitization. The redox-photosensitized reaction of **1b** with isopropylamine in the presence of DCNB using phenanthrene as a sensitizer gave **2g**, **3b**, and **4b** accompanied by the formation of *N*-isopropyl-9-amino-9,10-dihydrophenanthrene (**13**). When triphenylene was used as a sensitizer, the photoamination proceeded along with the consumption of triphenylene. Thus, the redox-photosensitized amination of **1b** using phenanthrene or triphenylene are inefficient because of the consumption of sensitizers.

In order to elucidate the stereochemistry of the addition of amines, the photoamination of 1-phenyl-3,4-dihydronaphthalene (**1c**) was performed. The photoamination of **1c** with ammonia, isopropylamine, and *t*-butylamine gave the corresponding *cis*- and *trans*-*N*-substituted 1-phenyl-2-amino-1,2,3,4-tetrahydronaphthalene (**14**, **15**, and **16**) (Scheme 6). The stereochemistries of **14**, **15**, and **16** were determined by their ^{1}H NMR spectra. The signal for the methine proton (H_A) on the C_1 of trans isomers appeared at 0.35—0.50 ppm higher in field than that of cis isomers. The upfield shift of H_A of trans isomers may be due to a shielding effect of lone-pair electrons on the adjacent nitrogen atom. Further support is that the vicinal coupling constants (J=5.0—5.5 Hz) between H_A and H_B in cis isomers were smaller than those in trans isomers (J=7.7—9.0 Hz). Though the ratio of the trans to cis isomer was dependent on the bulkiness of amine, the cis isomers (**15a** and **16a**) were



Scheme 5.



Scheme 6.

Table 2. Photoamination of 1-Phenyl-3,4-dihydronaphthalene (**1c**) with Ammonia and Alkylamines

Run	RNH_2	Products (**a** : **b**)[b]	Yield[a]	Conv. of **1**/%	Recov. of DCNB/%
15[c]	NH_3	**14** (49 : 51)	33	71	86
16	*i*-$PrNH_2$	**15** (75 : 25)	22	64	100
17	*t*-$BuNH_2$	**16** (79 : 21)	28	70	100

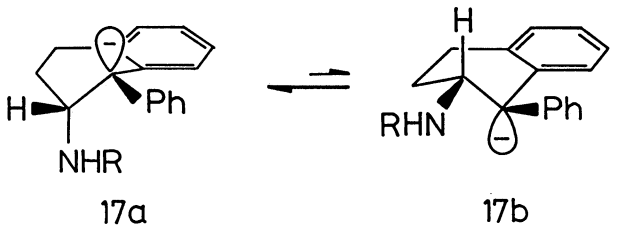
a) Isolated yields based on consumed **1c**. b) Isomer ratio of **a** to **b**. c) For MeCN-H_2O (9 : 1) solution.

mainly produced in the cases of photoamination with isopropylamine and *t*-butylamine (Table 2).

Discussion

The photochemical electron transfer reaction from electron-rich substances to aromatic nitriles has been well known to occur in polar solvents.[1] It is proposed that such photoamination is initiated by a photochemical electron transfer from **1** to DCNB, since no photoamination of **1** occurred in the absence of A (Eq. 1). The cation radicals of **1**, thus formed, react with RNH_2 to give aminated cation radicals which are reduced with the anion radical of DCNB and then protonated to afford **2** (Eq. 2).

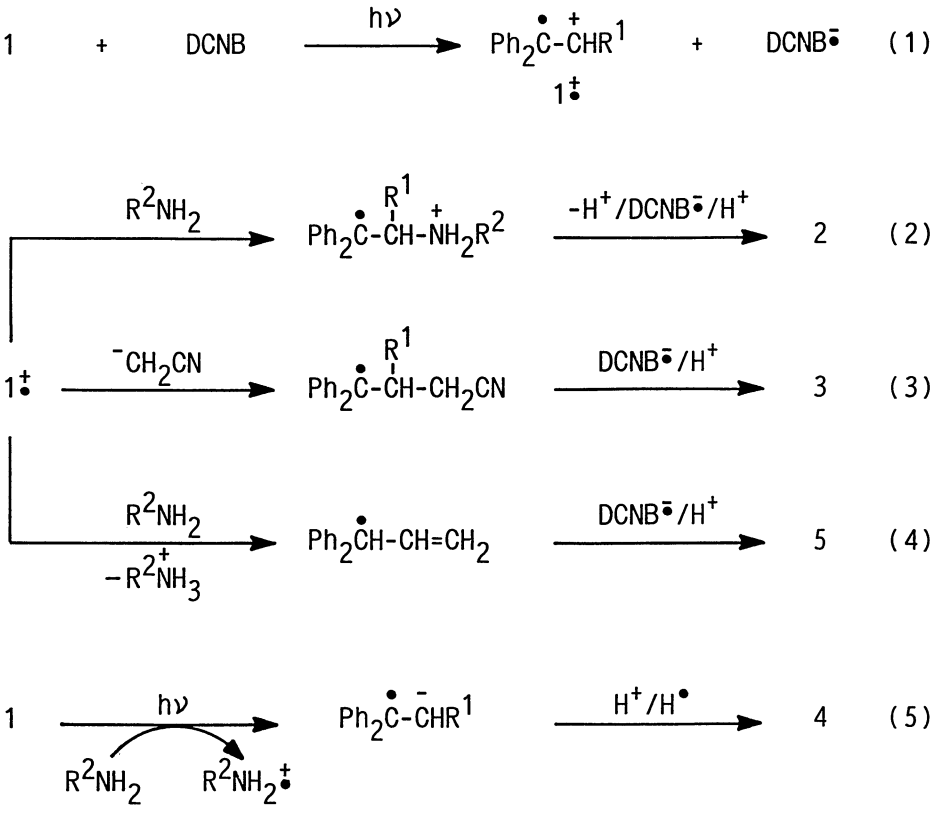
In the case of **1c**, the resulting aminated anion (**17**) takes both **17a** and **17b** conformations, depending on the bulkiness of the amine, as shown in Scheme 7.

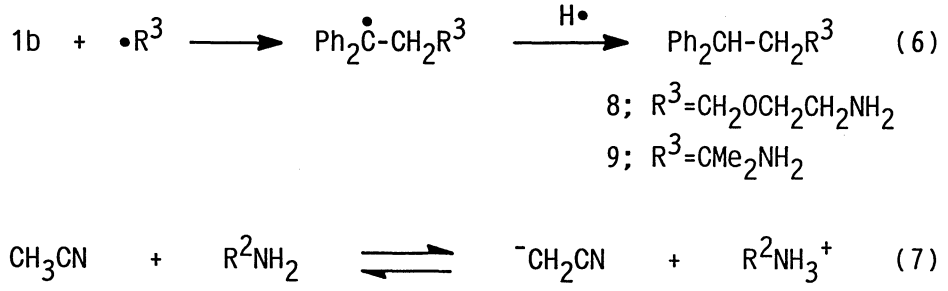


Scheme 7.

The electron pair of **17** may exist in the axial position, which is favorable for a maximum orbital overlap of the electron pair with the aromatic ring. When an amino group has a bulky alkyl group, a steric interaction between the amino group on C-2 and the phenyl group on C-1 may be expected to favor **17a**, in which the amino group is axial and phenyl group is equatorial. Therefore, the protonation of **17** affords mainly the cis isomer (**15a** and **16a**) in the photoamination of **1c** with isopropylamine or *t*-butylamine. This result is in accord with the results reported for the photoaddition of methanol to **1c**.[5]

The fact that 4,4-diphenyl-2,2-dideuterio-1-butanenitrile was formed from the photoamination of **1b** in acetonitrile-d_3 reveals that the cyanomethyl group of **3** can undoubtedly be attributed to acetonitrile. Figure 1 shows that **3b** is the primary product from the photoreaction of **1b**. On the other hand, it has been reported that **3** was not formed at all from the photoaddition of water and alcohols to **1a** or **1b** in the





Equation 1—7.

presence of electron acceptors.[5,6] Indeed, when DCNB was used as an electron acceptor, the photoaddition of water to **1b** in the absence of amines in acetonitrile gave only **7** in 41% yield without the formation of **3b**. This fact shows that the presence of amines is requisite for the formation of **3b**. These observations, therefore, suggest that $\mathbf{1}^{+\cdot}$ reacts with the cyanomethyl anion which is generated from the deprotonation of acetonitrile by the amine. The reduction of cyanomethylated radicals by the anion radical of DCNB gives **3** after protonation (Eqs. 3 and 7). Thus, $\mathbf{1}^{+\cdot}$ can undergo Eq. 3 competitively with Eq. 2, depending on the nature of RNH_2. *t*-Butylamine operates more effectively for the formation of **3** compared with other primary alkylamines since the bulky substituent may slow down the nucleophilic addition and/or the strong basicity may facilitate the deprotonation of acetonitrile. Also, amines operate as a base for the isomerization of **1a** to **5**, which proceeds by deprotonation from $\mathbf{1a}^{+\cdot}$ with RNH_2 according to Eq. 4.

The photoreaction of **1b** with isopropylamine in the absence of DCNB would be initiated by a photochemical electron transfer from isopropylamine to **1b** to give a cation radical of the amine and the anion radical of **1b**, as discussed in previous reports.[8,9,11] The protonation of the anion radical of **1b** and the subsequent hydrogen abstraction from such hydrogen sources as isopropylamine gave **4b** (Eq. 5). Equation 5 would take place to some extents, even for photoamination in the presence of DCNB, since a considerable amount of **4b** was produced.

The formation of **9** would occur by the reaction of **1b** with the 2-amino-2-propyl radical which is generated by deprotonation from the cation radical of isopropylamine or by hydrogen abstraction from isopropylamine with a radical species, as shown in Eq. 6. Similarly, the formation of **8** would occur by the reaction of **1b** with the 2-aminoethoxymethyl radical formed by hydrogen abstraction from 2-methoxyethylamine (Eq. 6). The formation of **3b** from the photoreaction in the absence of DCNB would occur by the reaction of **1b** with the cyanomethyl radical formed by hydrogen abstraction from acetonitrile by a radical species in reaction systems; this mechanism is in accord with that for photochemical incorporation of acetonitrile to norbornene.[11]

Degradation of secondary amines (**2b** and **2g**) to primary amines (**2a** and **2f**) can be attributed to be the consequence of secondary reactions, as is shown in Fig. 1. It was confirmed that the photoreaction of isolated **2g** with DCNB gave **2f**. Degradation would occur through an electron transfer reaction from **2b** or **2g** to the excited singlet state of DCNB.[9] Also, the formation of **6** occurred as a secondary reaction which proceeds by C-C bond cleavage of the cation radicals of **2a—e** generated by a photochemical electron transfer to DCNB. This is in agreement with a mechanism which has been reported for the cleavage of tertiary amines[12] and 2,2-diphenylethyl alkyl ethers.[13]

Neither DCA- nor CNN-photosensitization was a useful method for the photoamination of **1**. From the fluorescence quenching of DCA or CNN with **1** or amines, it was found that the excited singlet state of DCA or CNN was efficiently quenched by ammonia and primary amines, as well as by **1**. No occurrence of the DCA- or CNN-sensitized photoamination is caused by the more efficient quenching of the excited singlet state of DCA or CNN by RNH_2 than that by **1** under the reaction conditions.

Experimental

^1H and ^{13}C NMR spectra were taken on a Bruker AC 250P for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. The fluorescence and IR spectra were taken on a Hitachi MPF-4 and a JASCO A-302, respectively. A JEOL JMS-D300S was used for analyzing the mass spectra. GLC analysis was carried out on a Shimadzu GC-14A or a Hitachi 163 with flame-ionization detectors using a capillary column (CBP1-M25-025) or a 50 cm×4 mm column of 2% silicone OV-17 on Chromosorb WAW DMCS.

Spectral grade acetonitrile was distilled from P_2O_5 and then from CaH_2. 1,1-Diphenylethene, *p*-dicyanobenzene, and amines were commercially available. 1,1-Diphenylpropene was prepared from the acid-fragmentation of 2,2-diphenyl-3-methyloxetane prepared from the photoaddition of benzophenone with 2-butene.[14] 1-Phenyl-3,4-dihydronaphthalene was prepared according to a method described in the literature.[15]

Photoamination of 1a,b with Amines. Into a pyrex vessel was introduced an acetonitrile solution (150 ml) containing **1** (5.6 mmol) and DCNB (16 mmol). The amine (73

mmol) was added to the solution after argon bubbling for 50 min, whereas an ammonia solution was obtained by dissolving gaseous ammonia into the solution. The solutions were irradiated for 8—50 h with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex. After evaporation of the solvent, cool methanol was added to the residue and then unreacted DCNB was filtered off. The filtrate was chromatographed on silica gel with hexane to give **1**, **4**, **5**, and **6**. Further elution with hexane-benzene (4:1) gave **3**. The aminated products (**2a—i**) were obtained by elution with benzene-ethyl acetate (4:1) or acetone. Purification was carried out by either recrystallization from hexane-benzene or vacuum distillation. The recrystallization of **2c** and **2h**, however, could not be achieved owing to a failure regarding their acetylation. The structures of **2b**, **2d**, and **2e** were determined by comparisons of the ^{1}H and ^{13}C NMR spectra with authentic samples prepared from the reaction of 1,1-diphenyl-3-propanone with the corresponding amines in the presence of sodium cyanoborohydride.[16] The structures of **4a**, **4b**, **5**,[17] **6**, **7**, and **13**[2a] were determined by direct comparisons with authentic samples.

1-Methyl-2,2-diphenylethylamine (2a). The acetamide: Mp 113.0—113.5 °C; ^{1}H NMR δ=1.12 (3H, d, J=6.4 Hz), 1.80 (3H, s), 3.84 (1H, d, J=10.0 Hz), 4.83—4.93 (1H, m), 5.28 (1H, br d, J=8.5 Hz), and 7.16—7.29 (10H, m); ^{13}C NMR δ=20.4, 23.4, 47.4, 58.0, 126.72, 126.65, 128.1, 128.2, 128.6, 128.7, 141.8, 142.2, and 169.4; MS m/z 253 (M^+); IR ($CHCl_3$) 3430 and 1660 cm^{-1}; Found: C, 80.48; H, 7.29; N, 5.77%. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53%.

***N*-Isopropyl-(1-methyl-2,2-diphenylethyl)amine (2b):** ^{1}H NMR δ=0.98 (3H, d J=9.9 Hz), 1.00 (6H, d, J=10.0 Hz), 2.71 (1H, br s), 2.82—2.92 (1H, m), 3.54—3.65 (1H, m), 3.80 (1H, d, J=10.2 Hz), and 7.12—7.39 (10H, m); ^{13}C NMR J=18.7, 21.7, 24.2, 45.9, 53.2, 59.1, 126.4, 126.7, 128.3, 128.5, 128.8, 142.4, and 143.1; MS m/z 253 (M^+). The acetamide: Mp 161.5—162.0 °C; Found: C, 81.58; H, 8.46; N, 4.61%. Calcd for $C_{20}H_{25}NO$: C, 81.31 ; H, 8.53; N, 4.74%.

***N*-*t*-Butyl-(1-methyl-2,2-diphenylethyl)amine (2c):** ^{1}H NMR δ=0.96 (9H, s), 1.08 (3H, d, J=5.8 Hz), 3.54—3.65 (1H, m), 3.70 (1H, d, J=10.2 Hz), and 7.13—7.39 (10H, m); ^{13}C NMR δ=22.5, 29.9, 51.1, 60.3, 126.3, 126.8, 128.5, 128.6, 142.6, and 143.0; MS m/z 267 (M^+).

***N*-(2-Methoxyethyl)-(1-methyl-2,2-diphenylethyl)amine (2d):** ^{1}H NMR δ=1.00 (3H, d, J=6.1 Hz), 2.61—2.70 (1H, m), 2.78—2.88 (1H, m), 3.17 (3H, s), 3.27—3.39 (2H, m), 3.40—3.51 (1H, m), 3.76 (1H, d, J=10.2 Hz), and 7.09—7.38 (10H, m); ^{13}C NMR δ=18.5, 46.6, 55.8, 58.4, 59.3, 71.7, 126.3, 126.6, 128.1, 128.2, 128.5, 128.7, 142.4, and 143.3; MS m/z 269 (M^+).

***N*-(2-Hydroxyethyl)-(1-methyl-2,2-diphenylethyl)amine (2e):** Mp 83.5—84.0 °C; ^{1}H NMR δ=1.05 (3H, d, J=6.1 Hz), 2.63—2.72 (1H, m), 2.74—2.89 (3H, m), 3.46—3.57 (3H, m), 3.78 (1H, d, J=10.3 Hz), and 7.13—7.38 (10H, m); ^{13}C NMR δ=18.5, 48.1, 55.9, 59.0, 60.6, 126.5, 126.8, 128.0, 128.1, 128.6, 128.9, 142.2, and 142.8; MS m/z 255 (M^+).

2,2-Diphenylethylamine (2f). The acetamide: Mp 89.5—90.0 °C; ^{1}H NMR δ=1.82 (3H, s), 3.84 (1H, d, J=7.9 Hz), 3.86 (1H, d, J=7.9 Hz), 4.17 (1H, d, J=7.9 Hz), 5.67 (1H, br s), and 7.16—7.33 (10H, m); ^{13}C NMR δ=23.2 43.9, 50.5, 126.8, 128.0, 128.7, 141.9, and 170.2; MS m/z 239 (M^+). The acetamide of **2f** was unambiguously identified by a direct comparison with an authentic sample.

***N*-Isopropyl-2,2-diphenylethylamine (2g).** The acetamide: Mp 104.5—105.0 °C; ^{1}H NMR δ=0.78 and 1.18 (6H, d J=6.8 and 6.9 Hz), 1.58 and 2.10 (3H, s), 3.78 and 3.87 (2H, d, J=7.5 and 7.0 Hz), 3.74—3.82 and 4.11—4.20 (1H, m), 4.14 and 4.69 (1H, t, J=7.0 and 7.5 Hz), and 7.13—7.39 (10H, m); ^{13}C NMR δ=20.3 and 20.9, 22.3 and 22.6, 47.3 and 49.1, 48.4 and 51.6, 49.6 and 52.5, 126.3 and 126.9, 128.2 and 128.7, 128.6 and 132.7, 142.3 and 143.1, and 171.2; MS m/z 281 (M^+); IR ($CHCl_3$) 1620 cm^{-1}; Found: C, 80.79; H, 8.51; N, 5.07%. Calcd for $C_{19}H_{23}O$: C, 81.10; H, 8.24; N, 4.98%.

***N*-*t*-Butyl-2,2-diphenylethylamine (2h):** ^{1}H NMR δ=1.14 (9H, s), 3.28 (2H, d, J=8.0 Hz), 4.30 (1H, t, J=8.0 Hz), 4.70 (1H, br s), and 7.19—7.35 (10H, m); ^{13}C NMR δ=27.4, 46.9, 50.5, 52.1, 126.8, 128.0, 128.7, and 142.0; MS m/z 253 (M^+).

***N*-(2-Methoxyethyl)-2,2-diphenylethylamine (2i):** A colorless oil, ^{1}H NMR δ=2.81 (2H, t, J=5.3 Hz), 3.25 (2H, d, J=7.7 Hz), 3.30 (3H, s), 3.42 (2H, t, J=5.3 Hz), 4.21 (1H, t, J=7.7 H), and 7.14—7.38 (10H, m); ^{13}C NMR δ=49.1, 51.1, 54.5, 58.6, 71.7, 126.5, 127.9, 128.6, and 142.8; MS m/z 255 (M^+). The acetamide: Found: C, 76.98; H, 7.58; N, 4.98%. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71%.

3-Methyl-4,4-diphenylbutanenitrile (3a): Mp 55.0—55.5 °C; ^{1}H NMR δ=1.07 (3H, d, J=6.5 Hz), 2.10 (1H, dd, J=16.7 and 7.0 Hz), 2.33 (1H, dd, J=16.7 and 3.8 Hz), 2.62—2.79 (1H, m), 3.65 (1H, d, J=11.4 Hz), and 7.12—7.31 (10H, m); ^{13}C NMR δ=18.3, 23.5, 34.2, 57.6, 118.5, 126.6, 126.9, 127.6, 127.8, 128.7, 129.0, 142.5, and 142.6; MS m/z 235 (M^+); IR ($CHCl_3$) 2220 cm^{-1}.

4,4-Diphenylbutanenitrile (3b): ^{1}H NMR δ=2.20 (2H, t, J=7.5 Hz), 2.30—2.45 (2H, m), 4.03 (1H, t, J=7.9 Hz), and 7.10—7.31 (10H, m); ^{13}C NMR δ=15.7, 31.0, 49.8, 119.3, 126.8,127.7, 128.8, and 142.8; MS m/z 221 (M^+); IR ($CHCl_3$) 2190 cm^{-1}. The structure of **3b** was determined by a comparison with an authentic sample prepared from the cyanation of 3,3-diphenyl-1-propanol according to a reported method.[18]

1-(2-Aminoethoxy)-3,3-diphenylpropane (8). The acetamide: Mp 64.5—65.0 °C (from hexane-benzene); ^{1}H NMR δ=1.95 (3H, s), 2.28—2.36 (2H, m), 3.34—3.39 (6H, m), 4.09 (1H, t, J=7.9 Hz), 5.89 (1H, br s), and 7.15—7.37 (10H, m); ^{13}C NMR δ=23.2, 35.2, 39.3, 47.5, 69.1, 69.3, 126.3, 127.8, 128.5, 144.4, and 170.1; MS m/z 297 (M^+); IR ($CHCl_3$) 3440 and 1660 cm^{-1}; Found: C, 76.73; H, 7.63; N, 4.66%. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71%.

1,1-Dimethyl-3,3-diphenylpropylamine (9). The acetamide: Mp 120.5-121.0 °C (from hexane-benzene); ^{1}H MMR δ=1.29 (6H, s), 1.44 (3H, s), 2.53 (2H, d, J=7.1 Hz), 4.05 (1H, t, J=7.0 Hz), 5.38 (1H, br s), and 7.18—7.29 (10H, m); ^{13}C NMR δ=23.4, 27.3, 44.1, 47.2, 53.2, 125.6, 126.7, 128.1, 145.0, and 169.1; MS m/z 255 (M^+). IR ($CHCl_3$) 3440 and 1660 cm^{-1}; Found: C, 81.26; H, 8.46; N, 4.82%. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98%.

Photoreaction of 1b in *N,N*-Dimethylformamide. After irradiation, the photolysates were dissolved in 150 ml of benzene; then, *N,N*-dimethylformamide was extracted with six 50 ml portions of water. After evaporation of benzene, the residue was chromatographed on silica gel with hexane to give **1b** and **4b**. Further elution with benzene gave **10** and **11**. **12a** and **12b** were obtained by elution with benzene-ethyl acetate (8:1). **11** and **12b** could not be purified from the mixture of either **10** and **11** or **12a** and **12b**.

***N*-(3,3-Diphenylpropyl)-*N*-methylformamide (10):** Mp 60.0—61.0 °C (from hexane-benzene); ^{1}H NMR δ=2.30 and 2.33 (2H, m), 2.85 and 2.86 (3H, s), 3.17 and 3.28 (2H, t,

J=6.9 and 7.7 Hz), 3.86 and 3.94 (1H, t, J=7.9 and 7.8 Hz), 7.14—7.33 (10H, m), 7.60 and 7.98 (1H, s); ^{13}C NMR δ=29.4 and 32.5, 33.5 and 34.7, 43.5 and 47.6, 48.0 and 49.1, 126.4 and 126.7, 127.6 and 127.7, 128.6 and 128.8, 143.5 and 144.1, 162.4 and 162.8; MS m/z 253 (M^+); IR ($CHCl_3$) 1665 cm^{-1}; Found: C, 80.65; H, 7.53; N, 5.79%. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53%.

***N,N*-Dimethyl-3,3-diphenylpropanamide (11):** ^{1}H NMR δ=2.86 (6H, s), 3.04 (2H, d, J=7.5 Hz), 4.68 (1H, t, J=7.4 Hz), and 7.13—7.32 (10H, m); ^{13}C NMR δ=35.5, 37.2, 39.3, 47.2, 126.3, 127.8, 128.8, 144.3, and 171.2; MS m/z 253 (M^+); IR ($CHCl_3$) 1645 cm^{-1}.

***N*-(4-Cyanobenzyl)-*N*-methylformamide (12a):** A colorless oil, ^{1}H NMR δ=2.80 and 2.91 (3H, s), 4.49 and 4.58 (2H, s), 7.35—7.38 (2H, d, J=8.0 Hz), 7.64—7.69 (2H, d, J=8.0 Hz), 8.20 and 8.26 (1H, s); ^{13}C NMR δ=29.7 and 34.3, 47.6 and 53.0, 111.6 and 112.2, 118.3 and 118.6, 128.0 and 128.7, 132.5 and 132.8, 141.5 and 141.7, 162.78 and 162.82; MS m/z 174 (M^+); IR ($CHCl_3$) 2230 and 1660 cm^{-1}; Found: C, 68.84; H, 5.89; N, 16.26%. Calcd for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.79; N, 16.08%.

***N*-(3-Cyanobenzyl)-*N*-methylformamide (12b):** ^{1}H NMR δ=2.83 and 2.96 (3H, s), 4.64 and 4.77 (2H, s), 7.27—7.50 (2H, m), 7.57—7.74 (2H, m), 8.20 and 8.34 (1H, s); ^{13}C NMR δ=29.6 and 34.5, 45.8 and 51.4, 112.1 and 112.3, 116.9 and 117.4, 128.3 and 128.8, 128.9 and 132.6, 132.8 and 133.4, 139.5 and 139.9, 162.9 and 163.0; MS m/z 174 (M^+); IR ($CHCl_3$) 2230 and 1660 cm^{-1}.

Photoamination of 1c. In a similar manner to the case of **1a**, the photoamination of **1c** was performed for an acetonitrile solution (50 ml) containing **1c** (2.5 mmol), DCNB (2.5 mmol), and the amine (25 mmol). After irradiation, aminated products were obtained by extraction with dilute hydrochloric acid. The acidic aqueous layer was basified with saturated $NaHCO_3$ followed by extraction with diethyl ether. Evaporation of the ether left crude aminated products. **1c** and DCNB were recovered from benzene solutions and were chromatographed on silica gel with hexane and benzene. A mixture of **14a** and **14b** was acetylated with Ac_2O, and recystallized from hexane-benzene to give the acetamide of **14a**. Also, **15a** was obtained in the same way, though the acetamide of **16** was not purified by recrystallization.

***cis*-2-Amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (14a):** ^{1}H NMR δ=1.62 (2H, br s), 2.03—2.15 (2H, m), 2.88—3.12 (2H, m), 3.32 (1H, ddd, J=8.1, 5.4, and 5.2 Hz), 4.22 (1H, d, J=5.2 Hz), and 6.68—7.40 (9H, m); ^{13}C NMR δ=28.3, 31.0, 51.7, 56.1, 125.9, 126.3, 126.5, 127.9, 128.5, 130.6, 130.8, 136.3, 138.3, and 141.7.

***trans*-2-Amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (14b):** ^{1}H NMR δ=1.62 (2H, br s), 1.72—1.85 (2H, m), 2.88—3.12 (2H, m) 3.20 (1H, ddd, J=10.4, 9.0, and 3.0 Hz), 3.73 (1H, d, J=9.0 Hz), and 6.68—7.40 (9H, m); ^{13}C NMR δ=28.0, 28.5, 50.5, 54.5, 125.9, 126.0, 126.7, 128.6, 128.7, 129.6, 130.2, 136.3, 138.8, and 144.4. The acetamide: Mp 196.5—198.0 °C; Found: C, 81.41; H, 7.32; N, 5.16%. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28%.

***cis*-*N*-Isopropyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (15a):** ^{1}H NMR δ=1.00 (3H, d, J=6.0 Hz), 1.03 (3H, d, J=6.0 Hz), 1.26 (1H, br s), 1.57—1.83 (2H, m), 3.00—3.05 (2H, m), 3.12 (1H, q, J=6.0 Hz), 3,21 (1H, ddd, J=11.7, 5.0, and 3.3 Hz), 4.36 (1H, d, J=5.0 Hz), and 6.92—7.37 (8H, m); ^{13}C NMR δ=23.0, 23.1, 25.0, 28.9, 44.4, 48.5, 53.3, 125.8, 126.3, 127.8, 128.6, 130.5, 130.8, 136.6, 139.0, and 141.9.

***trans*-*N*-Isopropyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (15b):** ^{1}H NMR δ=0.82 (3H, d, J=6.2 Hz), 1.01 (3H, d, J=6.2 Hz), 1.26 (1H, br s), 2.05—2.14 (2H, m), 2.80—2.92 (2H, m), 3.00—3.05 (1H, m), 3,06—3.09 (1H, m), 3.91 (1H, d, J=7.7 Hz), 6.74 (1H, d, J=7.7 Hz), and 6.92—7.37 (8H, m); ^{13}C NMR δ=22.4, 24.2, 26.9, 27.3, 45.6, 52.6, 57.4, 125.9, 126.0, 126.5, 128.4, 128.5, 129.4, 130.7,136.6, 138.4, and 144.7. The acetamide: Mp 143.5—145.0 °C; Found: C, 82.24; H, 7.93; N, 4.61%. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56%.

***cis*-*N*-*t*-Butyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (16a):** ^{1}H NMR δ=1.09 (9H, s), 1.40 (1H, br s), 1.61—1.91 (2H, m), 2.99—3.05 (2H, m), 3.20 (1H, ddd, J=11.6, 5.5, and 3.5 Hz), 4.12 (1H, d, J=5.5 Hz), 6.91 (1H, d, J=7.7 Hz), and 7.03—7.36 (8H, m); ^{13}C NMR δ=28.6, 29.1, 30.0, 50.8, 51.0, 51.5, 125.7, 126.2, 126.2, 127.6, 128.6, 130.8, 131.0, 136.5, 139.5, and 142.5.

***trans*-*N*-*t*-Butyl-2-amino-1-phenyl-1,2.3,4-tetrahydronaphthalene (16b):** ^{1}H NMR δ=0.87 (9H, s), 1.40 (1H, br s), 2.13—2.24 (2H, m), 2.93 (2H, t, J=5.0 Hz), 2.99—3.05 (1H, m), 3.77 (1H, d, J=9.0 Hz), 6.73 (1H, d, J=7.5 Hz), and 7.03—7.36 (8H, m); ^{13}C NMR δ=28.3, 29.8, 30.0, 51.0, 54.2, 55.4, 125.7, 126.0, 126.6, 127.7, 128.4, 129.8, 130.9, 137.0, 139.2, and 144.7.

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