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Photoinduced Nucleophilic Addition of Ammonia and Alkylamines to Methoxy-Substituted Styrene Derivatives

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Abstract: The photoaminations of *trans*-1-arylpropenes (aryl = 2-methoxyphenyl (**1**), 3-methoxyphenyl (**2**), 3,4-dimethoxyphenyl (**3**), and 4-methoxyphenyl (**4**)) with NH_3, *i*-$PrNH_2$, and *t*-$BuNH_2$ (RNH_2) in the presence of *p*-dicyanobenzene (*p*-DCB) gave 2-alkylamino-1-arylpropanes (**9**) and/or 2-alkylamino-1-aryl-1-(4-cyanophenyl)propanes (**10**). The photoaminations of 1,2-dihydro-7-methoxynaphthalenes (**6-8**) with RNH_2 in the presence of *p*-DCB gave mainly 2-alkylamino-1-(4-cyanophenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalenes (**13**). The photoamination of *trans*-1-(3,5-dimethoxyphenyl)propene (**5**) with *i*-$PrNH_2$ occurred at aromatic ring to give *trans*-1-(2-isopropylamino-3,5-dimethoxyphenyl)propene (**11**). The photoaminations of **1-4** and **6-8** with NH_3 in the presence of *m*-dicyanobenzene gave the aminated products without incorporation of cyanophenyl group. Furthermore, the addition of 1,3,5-triphenylbenzene and *m*-terphenyl for these reactions improved the yields of the photoaminated products.

INTRODUCTION

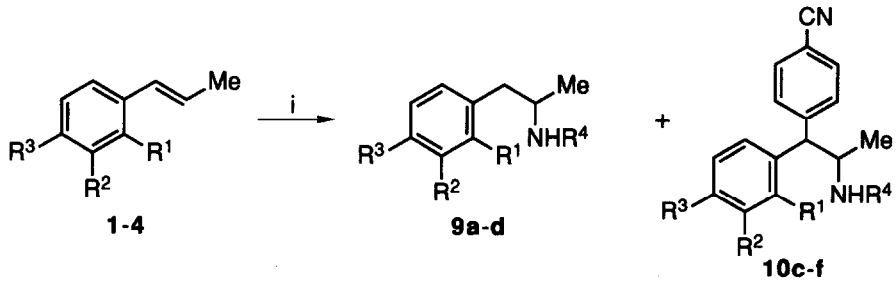
Photoinduced nucleophilic addition (PNA) has received much attention as a potentially useful procedure for organic synthesis.[1] Since first report on the PNA of MeOH to 1,1-diphenylethene by Arnold in 1973,[2] PNA of a variety of aryl-substituted olefins[3] and strained compounds[4] concerning the products analysis, the selectivity, the efficiency, the additive effect,[3g,4e,g] the solvent effect,[3k] and the mechanism[3i] have been widely investigated. Most of these works have been performed by use of alcohols as a nucleophile, it has been shown that photosensitizations with 9,10-dicyanoanthracene,[3h,i,k,4g,i] 1-cyanonaphthalene,[3a,d,e,4b,c,h] or 1,4-dicyanonaphthalene[3j,l] were a useful method for the efficient PNA of alcohols to the substrates which have only weak or no absorption at longer wavelength. However, our previous studies on the PNA of ammonia and amines *(photoamination)* have elucidated that the photosensitization with these aromatic nitriles were not effective for the photoamination of arenes,[5a-c] 1,1-diarylalkenes,[5d] and stilbenes,[5e] since these sensitizers in the excited state were quenched efficiently by ammonia and amines.. In order to apply the photoamination extensively, this paper reports our new method for efficient photoamination of styrene derivatives.[6]

RESULTS AND DISCUSSION

Photoamination

We selected methoxy-substituted *trans*-1-phenylpropenes (**1-5**) and 7-methoxy-1,2-dihydronaphthalenes (**6-8**) which have relatively low oxidation potentials so that the photoinduced electron transfer from these substrates to *m*- or *p*-dicyanobenzene (*m*- or *p*-DCB) would proceed efficiently. The photoaminations of **1-8** (D) with ammonia and alkylamines (RNH_2) were performed by irradiating a deaerated MeCN-H_2O or MeCN solution containing D, *m*- or *p*-DCB, and RNH_2 by a high-pressure mercury lamp through a Pyrex filter under cooling with water (Scheme 1).

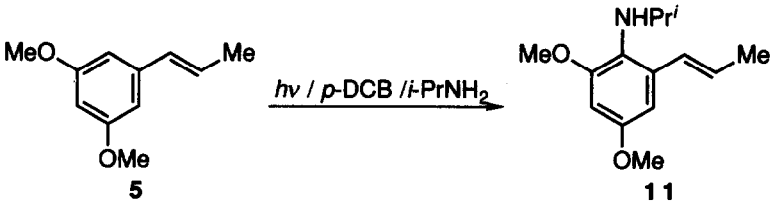
The results using *p*-DCB are summarized in Table 1. The photoaminations of *trans*-1-(2-methoxyphenyl)-propene (**1**) and *trans*-1-(3-methoxyphenyl)propene (**2**) with NH_3 gave 2-amino-1-arylpropanes (**9a** and **9b**), respectively, as sole product. The photoaminations of *trans*-1-(3,4-dimethoxyphenyl)propene (**3**) and *trans*-1-(4-methoxyphenyl)propene (**4**) with NH_3 gave 2-amino-1-arylpropanes (**9c** and **9d**), accompanying the formation of 2-amino-1-aryl-1-(4-cyanophenyl)propanes (**10c** and **10d**) which were formed from the incorporation of both *p*-cyanophenyl group and amino group into olefinic moiety. The photoaminations of **4** with *i*-$PrNH_2$ and *t*-$BuNH_2$ gave only 2-alkylamino-1-(4-cyanophenyl)-1-(4-methoxyphenyl)propanes (**10e** and **10f**). In contrast to the above photoamination, the photoamination of *trans*-1-(3,5-dimethoxyphenyl)-



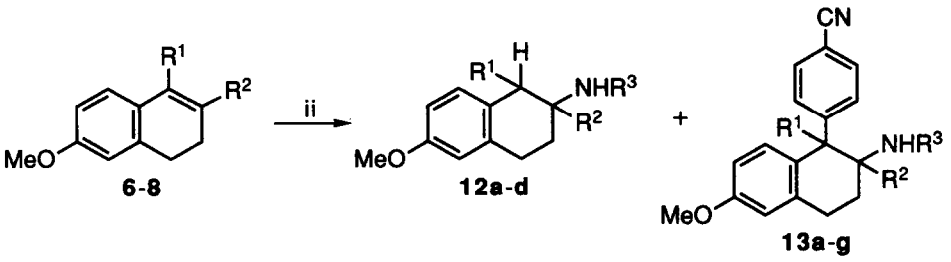
1: R^1 = OMe; R^2 = R^3 = H
2: R^2 = OMe; R^1 = R^3 = H
3: R^2 = R^3 = OMe; R^1 = H
4: R^3 = OMe; R^1 = R^2 = H

a: R^1 = OMe; R^2 = R^3 = R^4 = H
b: R^2 = OMe; R^1 = R^3 = R^4 = H
c: R^2 = R^3 = OMe; R^1 = R^4 = H
d: R^3 = OMe; R^1 = R^2 = R^4 = H
e: R^3 = OMe; R^1 = R^2 = H; R^4 = *i*-Pr
f: R^3 = OMe; R^1 = R^2 = H; R^4 = *t*-Bu

Scheme 1. Reagent i: *hν* / DCB / R^4NH_2



Scheme 2.



6: $R^1 = R^2 = H$
7: $R^1 = Me$; $R^2 = H$
8: $R^1 = H$; $R^2 = Me$

a: $R^1 = R^2 = R^3 = H$
b: $R^1 = R^2 = H$; $R^3 = i$-Pr
c: $R^1 = R^2 = H$; $R^3 = t$-Bu
d: $R^1 = Me$; $R^2 = R^3 = H$
e: $R^1 = Me$; $R^2 = H$; $R^3 = i$-Pr
f: $R^1 = Me$; $R^2 = H$; $R^3 = t$-Bu
g: $R^1 = R^3 = H$; $R^2 = Me$

Scheme 3. Reagent ii: $h\nu$ / DCB / R^3NH_2

Table 1. Photoamination of Methoxy-Substituted Styrene Derivatives (**1-8**) with NH_3 in the Presence of *p*-DCB[a]

substrate ($E_{1/2}^{ox}$ (V))[b]	RNH_2	irradn. time (h)	product yield[c] (%)			conv. of **1-8** (%) [d]	recov. of *p*-DCB (%)
1 (0.86)	NH_3	4	**9a** 68			92	93
2 (1.18)	NH_3	18	**9b** 28			91	93
3 (0.82)	NH_3	20	**9c** 29	**10c**	2 (1:0)	67	77
4 (0.93)	NH_3	9	**9d** 8	**10d**	37 (1:0.7)	100	50
4	i-$PrNH_2$	3		**10e**	20 (1:0)	67	80
4	t-$BuNH_2$	3		**10f**	29 (1:0.2)	99	51
5 (1.10)	i-$PrNH_2$	15	**11** 57			100	77
6 (0.82)	NH_3	8	**12a** 6	**13a**	37 (1:0)	97	51
6	i-$PrNH_2$	8		**13b**	72 (1:1)	100	19
6	t-$BuNH_2$	6		**13c**	49 (1:0)	100	45
7 (0.78)	NH_3	8	**12d** 9 (1:1)	**13d**	41 (1:0)	83	51
7	i-$PrNH_2$	6		**13e**	76 (1:0)	100	24
7	t-$BuNH_2$	12		**13f**	50 (1:0)	100	36
8 (0.69)	NH_3	10		**13g**	18 (1:0)	88	59

[a] Irradiation of an ammonia-saturated MeCN-H_2O (9:1; 70 ml) solution containing **1-4**, **6-8** (3.5 mmol), *p*-DCB (3.5 mmol), or a deaerated MeCN solution (70 ml) containing **4-7** (3.5 mmol), *p*-DCB (3.5 mmol), and the amine (17.5 mmol). [b] Oxidation potentials vs. Ag/NO_3. [c] Isolated yields based on the consumed substrates. The values in parenthesis are isomer ratio. [d] After the photoreaction, **1-4** were recovered as *cis* and *trans*-isomers.

propene (**5**) occurred at aromatic ring to give *trans*-1-(2-isopropylamino-3,5-dimethoxyphenyl)propene (**11**) (Scheme 2). The propenyl group of **11** was confirmed to keep the *trans* configuration. No indication was obtained for the significant formation of other products occurring from the addition of the amine to the propenyl group. The photoaminations of 7-methoxy-1,2-dihydronaphthalene (**6**), 7-methoxy-4-methyl-1,2-dihydronaphthalene (**7**), and 7-methoxy-3-methyl-1,2-dihydronaphthalene (**8**) with NH_3, *i*-$PrNH_2$, and *t*-$BuNH_2$ gave mainly 2-alkylamino-1-(4-cyanophenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalenes (**13a-g**) (Scheme 3).

When *m*-DCB was used as an electron acceptor in place of *p*-DCB, the photoamination of **4** with NH_3 entirely suppressed the formation of **10d** to increase the formation of **9d** from 8 % to 52 % yield (Tables 1 and 2). Similarly, the selective photoaminations of **3**, **6**, **7**, and **8** with NH_3 occurred in the presence of *m*-DCB to give **9c**, **12a**, **12d**, and **12g**, respectively. Furthermore, the yield of **9d** was remarkably improved by the addition of 1,3,5-triphenylbenzene (TPB) or *m*-terphenyl (*m*-TP), while the addition of 1,2,4-triphenylbenzene (1,2,4-TPB), *p*-terphenyl (*p*-TP), or biphenyl (BP) was not so effective, as shown in Table 2. After the photoreaction, these polyphenylbenzenes (ArH) were recovered in high yields without the reaction with NH_3. Also, the yields of **9a-c**, **12a**, **12d**, and **12g** in the photoaminations of **1-3**, **6-8** with NH_3 were, to some extents, improved by the addition of TPB.

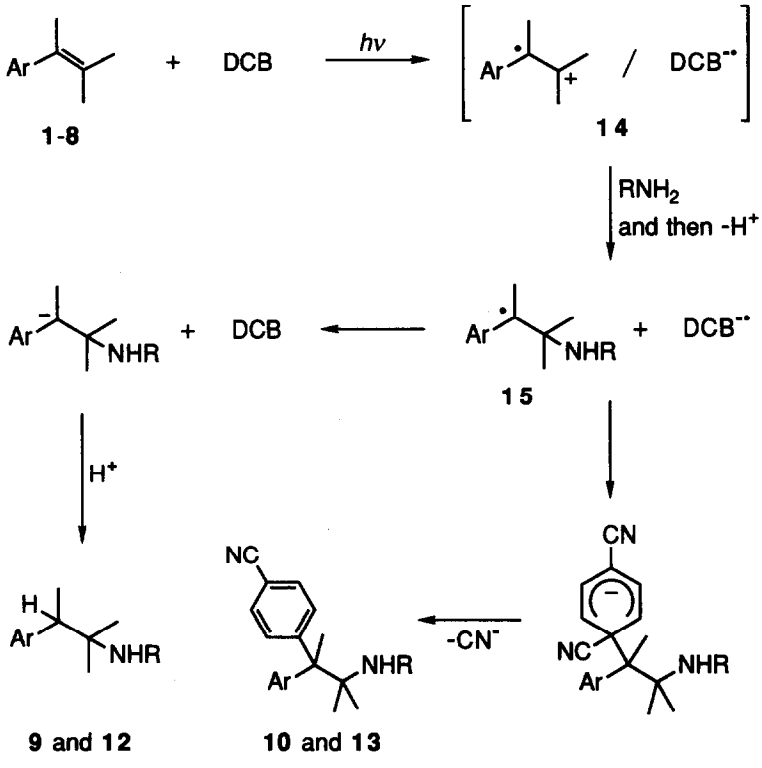
Table 2. Additive Effects of Polyphenylbenzenes (ArH) to Photoamination of Styrene Derivatives (**1-4**, **6-8**) with NH_3 in the Presence of *m*-DCB[a]

substrate	ArH[b]	irradn. time (h)	product yield[c] (%)		conv. of **1-8** (%)[d]	recov. of *m*-DCB (%)	recov. of ArH (%)
1[e]	TPB	4	**9a**	75	92	100	95
2[e]	TPB	24	**9b**	46	93	98	87
3	TPB	18	**9c**	65	100	96	83
4	none	4	**9d**	52	95	87	-
4	TPB	4	**9d**	91	98	82	68
4	*m*-TP	5	**9d**	85	98	95	99
4	1,2,4-TPB	6	**9d**	67	87	96	98
4	*p*-TP	4	**9d**	66	97	90	96
4	BP	6	**9d**	58	100	90	72
6	none	8	**12a**	23	100	67	-
6	TPB	8	**12a**	29	100	58	72
7	none	10	**12d**	25 (1:0.7)	90	69	-
7	TPB	6	**12d**	35 (1:0.7)	90	73	90
8	none	10	**12g**	42	86	37	-
8	TPB	6	**12g**	48	89	80	83

[a] Irradiation of an ammonia-saturated MeCN-H_2O (9:1; 75 ml) solution containing substrate (2 mmol), DCB (3.75 mmol), and additive (ArH; 0.75 mmol). [b] TPB = 1,3,5-triphenylbenzene; *m*-TP = *m*-terphenyl; 1,2,4-TPB = 1,2,4-triphenylbenzene; *p*-TP = *p*-terphenyl; BP = biphenyl. [c] Isolated yields based on consumed substrates. The values in parenthesis are isomer ratio. [d] After the photoreaction, **1-4** were recovered as *cis* and *trans*-isomers. [e] Using *p*-DCB as an electron acceptor.

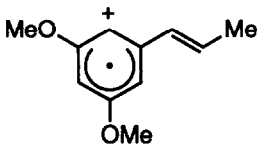
Mechanism

In a similar manner as the photoamination of arenes,[5a-c] 1,1-diarylalkenes,[5d] and stilbenes[5e] reported so far, the photoamination of **1-8** (D) is initiated by electron transfer from the excited singlet state of D to DCB, since the oxidation potentials of D were relatively low, as shown in Table 1, and no photoamination of D occurred in the absence of DCB. Although the fluorescences of *m*- and *p*-DCB by RNH_2 were quenched at nearly diffusional-controlled rates, the electron transfer from RNH_2 to the excited singlet state of DCB does not participate in this photoamination, since incident light was almost absorbed not by DCB but by D under these reaction conditions: the molar extinction coefficients at 300 nm (ε_{300}) of **4** and *p*-DCB were 7×10^3 and 43 dm^3 mol^{-1} cm^{-1}, respectively. It is assumed that the resulting cation radicals of D exist in the form of radical ion pairs (**14**) with the anion radical of DCB rather than free cation radicals (Scheme 4). Nucleophilic addition of RNH_2 to **14** occurs to give the aminated radicals (**15**) after deprotonation. The one-electron reduction of **15** with $DCB^{-\bullet}$ followed by protonation gives the aminated products, **9** and **12**. Moreover, the formations of **10** and **13** can be easily interpreted in terms of the radical-radical anion coupling between **15** and *p*-$DCB^{-\bullet}$, as reported for other PNA.[4a,f,k,7] The facile coupling in **4** and **6-8** can be attributed to the fact that it is hard to reduce **15** by *p*-$DCB^{-\bullet}$ owing to strong electron-donating ability of methoxyl group.



Scheme 4.

The regioselectivity of the photoamination can be related to the distribution of positive charge in cation radicals of substrates, as reported in the photoamination of stilbenes.[5e] The positive charge of the cation radicals of **1**-**4** and **6**-**8** might develop to some extents over olefinic moiety, resulting in the amination at propenyl group. On the other hand, the positive charge in $5^{+\cdot}$ develops mainly over aromatic nuclei where two methoxyl groups may highly stabilize the positive charge, because of the occurrence of the selective photoamination at aromatic nuclei and the lack of isomerization of propenyl group.



$5^{+\cdot}$

Additive Effect of Polyphenylbenzenes

It is well known that aromatic hydrocarbons work as π-donor that can interact with a cation radical.[3b,f,8] Here, several polyphenylbenzenes (ArH) were selected as π-donor, since the cation radicals of polycyclic arenes such as phenanthrene were added easily by NH_3.[5a] Table 3 shows the oxidation potentials, the fluorescence lifetime, and the molar extinction coefficients of ArH used. The oxidation potentials of all ArH were much higher than that of D, revealing no occurrence of the hole transfer from the cation radicals of D to ArH. In the case of the photoamination of **4** in the presence of 1,2,4-TPB, *p*-TP, or BP of which ε_{300} were similar to that of **4**, incident light was absorbed by both ArH and **4** under these reaction conditions. On the other hand, in the case of the photoamination of **4** in the presence of TPB or *m*-TP, incident light was almost absorbed not by TPB or *m*-TP but by **4**, because ε_{300} of TPB and *m*-TP were smaller than that of **4**. Therefore, the photoinduced electron transfer occurred mainly from the excited singlet state of **4** to DCB even in the presence of TPB or *m*-TP, revealing that effective ArH such as TPB and *m*-TP did not participate in the photoinduced electron transfer.

It can be assumed that the additive effect of TPB or *m*-TP comes from the formation of π-complex (**16**) with $D^{+\cdot}$ of **14**. The localized cation radicals of styrenes and 1,1-diphenylethene[3i] are highly reactive compared with the delocalized cation radicals such as the cation radicals of arenes.[5b] Therefore, the localized cation radicals tend to cause side reactions involving dimerization, deprotonation, and isomerization, resulting in the amination in lower yields compared with the delocalized cation radicals. The π-complex formation would lower the reactivity of **14** and suppress the side reactions, resulting in the effective amination. A similar effect due to π-complex formation was observed in the photoamination of stilbenes in which the yields of the aminated products were improved by use of benzene as co-solvent.[5d]

$$\mathbf{14} + \mathrm{ArH} \longrightarrow \underset{\mathbf{16}}{[\mathrm{D} / \mathrm{ArH}]^{+\cdot}} + \mathrm{DCB}^{-\cdot}$$

BP has been used as a cosensitizer for 9,10-dicyanoanthracene (DCA)-photosensitized oxygenation: the cation radicals of BP ($BP^{+\cdot}$) generated by photoinduced electron transfer from BP to DCA produce efficiently the cation radicals of substrates by a hole transfer from $BP^{+\cdot}$ to substrates.[9] However, the present additive effect of TPB or *m*-TP is different from that of the cosensitizer, because the yields of the aminated products were not improved by the addition of BP, although the cation radicals of BP might be formed by photoinduced

electron transfer from BP to DCB. Probably a hole transfer from $BP^{+\bullet}$ to **4** is inefficient because of reduction of $BP^{+\bullet}$ by NH_3.

Table 3. Oxidation Potentials and Spectral Data of Polyphenylbenzenes (ArH)

ArH	$E_{1/2}^{ox}$ (V)[a]	τ_f (ns)[b]	ε_{300}[c] $\times 10^{-3}$
TPB	1.52	42	0.8
m-TP	1.52	4	2.3
1,2,4-TPB	1.54	2	5.2
p-TP	1.51	2	17.3
BP	1.45[d]	16	5.0

[a] The oxidation potentials vs. $Ag/AgNO_3$ in MeCN. [b] Fluorescence lifetime in MeCN. [c] Molar extinction coefficient at 300 nm. [d] The value from ref. 9f.

CONCLUSION

The photoaminations show different features from the PNA of MeOH, because of the lower oxidation potential, stronger nucleophilicity, and stronger basicity of RNH_2 compared with those of alcohols. For example, the arenes such as phenanthrene and anthracene underwent photoamination but did not undergo PNA of MeOH. As mentioned above, DCA, CNN, and DCN-photosensitizations could not apply to the photoamination because of the efficient quenching of the excited sensitizer with RNH_2, although these photosensitizations were employed to improve the efficiency of the PNA of other nucleophiles such as alcohols, cyanide ion[3a,4b,10] and carboxylic acid.[11] Also, the redox-photosensitizations[3b,f] which were reported to the PNA of indene and furan using phenanthrene as a sensitizer could not be applied to the photoamination, owing to the lower oxidation potential and stronger nucleophilicity of RNH_2. Therefore, the present additive effect of π-donor will be a suitable method to enhance the yield of photoamination. Moreover, the present amination will be a useful tool for the preparation of phenethylamines and aminotetralin derivatives which have medicinal interests.[12]

EXPERIMENTAL

Melting points were determined with a Sibata MEL-270 and are uncorrected. ^1H and ^{13}C NMR spectra were taken on a Bruker AC 250P for $CDCl_3$ solutions using tetramethylsilane as an internal standard. MS spectra were taken on a Hitachi 2000A. GLC analysis was performed on a Shimadzu GC-14A using a capillary column. Oxidation potentials were measured for a MeCN solution containing Et_4NBF_4 (0.1 M) at a scan rate of 0.5 V/s on a Hokuto Denko HA-501G and HB-105 using $Ag/AgNO_3$ as a reference electrode.

Materials

Acetonitrile of spectral grade was distilled from CaH_2 before use. *m*- and *p*-Dicyanobenzenes were recrystallized from MeOH. *trans*-1-(4-Methoxyphenyl)propene (**4**) was distilled before use. 1-Arylpropenes

(**1-3, 5**) were prepared from the Grignard reaction of EtMgBr with the corresponding benzaldehydes followed by dehydration with *p*-toluenesulfonic acid and then the *trans*-isomers were separated by column chromatograph on silica gel.

***trans*-1-(2-Methoxyphenyl)propene (1)**: Oil, bp 85 °C / 1 mmHg. ^{1}H NMR δ 1.89 (dd, J = 6.6, 1.7 Hz, 3H), 3.82 (s, 3H), 6.14-6.28 (m, 1H), 6.72 (dd, J = 15.8, 1.6 Hz, 1H), 6.82-7.04 (m, 2H), 7.13-7.22 (m, 1H), 7.38 (d, J = 7.5 Hz, 1H). ^{13}C NMR δ 18.92, 55.43, 110.75, 120.66, 125.67, 126.46, 126.51, 127.74, 135.92, 156.19. Exact mass. Calcd for $C_{10}H_{12}O$: 148.0888. Found: 148.0890.

***trans*-1-(3-Methoxyphenyl)propene (2)**: Oil, ^{1}H NMR δ 1.87 (dd, J = 6.2, 1.2 Hz, 3H), 3.80 (s, 3H), 6.15-6.29 (m, 1H), 6.37 (d, J = 16.8 Hz, 1H), 6.74 (dd, J = 8.1, 2.3 Hz, 1H), 6.86-6.93 (m, 2H), 7.16-7.24 (m, 1H). ^{13}C NMR δ 18.44, 31.24, 55.17, 111.26, 112.37, 118.54, 126.07, 129.43, 130.97, 139.46, 159.82. Exact mass. Calcd for $C_{10}H_{12}O$: 148.0888. Found: 148.0891.

***trans*-1-(3,4-Dimethoxyphenyl)propene (3)**: Oil, ^{1}H NMR δ 1.85 (d, J = 6.5 Hz, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 6.02-6.16 (m 1H), 6.33 (d, J = 15.7 Hz, 1H), 6.79-6.88 (m, 3H). ^{13}C NMR δ 18.12, 55.53, 55.67, 108.31, 111.01, 118.45, 123.51, 130.42, 130.95, 147.96, 148.78. Exact mass. Calcd for $C_{11}H_{14}O_2$: 178.0992. Found: 178.0973.

***trans*-1-(3,5-Dimethoxyphenyl)propene (5)**: Mp 57.0-58.0 °C (from methanol). ^{1}H NMR δ 1.87 (d, J = 5.8 Hz, 3H), 3.78 (s, 6H), 6.15-6.37 (m, 3H), 6.49 (d, J = 2.1 Hz, 2H). ^{13}C NMR δ 18.41, 55.24, 99.05, 103.92, 126.31, 131.00, 140.00, 160.86. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92 %. Found: C, 74.21; H, 7.94 %.

7-Methoxy-1,2-dihydronaphthalene (**6**) was prepared from the reaction of 6-methoxy-1-tetralone with *p*-toluenesulfonylhydrazide and subsequent treatment with butyllithium[13]. **6**: Oil, bp 103.0-106.0 °C / 1 mmHg. ^{1}H NMR δ 2.23-2.32 (m, 2H), 2.76 (t, J = 8.0 Hz, 2H), 3.78 (s, 3H), 5.88 (dt, J = 9.5, 4.4 Hz, 1H), 6.41 (d, J = 9.5 Hz, 1H), 6.66-6.68 (m, 2H), 6.93 (d, J = 9.0 Hz, 1H). ^{13}C NMR δ 23.00, 28.04, 55.24, 111.06, 113.83, 125.94, 126.86, 127.15, 127.39, 137.20, 158.58. Exact mass. Calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0883.

7-Methoxy-4-methyl-1,2-dihydronaphthalene (**7**) and 7-methoxy-3-methyl-1,2-dihydronaphthalene (**8**) were prepared from the reaction of MeMgBr with 6-methoxy-1-tetralone and 6-methoxy-2-tetralone, respectively, followed by dehydration by heating with Ac_2O. **7**: Oil, bp 108 °C / 1 mmHg. ^{1}H NMR δ 2.02 (d, J = 1.52 Hz, 3H), 2.20-2.26 (m, 2H), 2.73 (t, J = 7.8 Hz, 2H), 3.79 (s, 3H), 5.71 (br s, 1H), 6.70 (s, 1H), 6.70-6.74 (m, 1H), 7.14 (d, J = 8.9 Hz, 1H). ^{13}C NMR δ 19.36, 23.17, 28.87, 55.21, 110.76, 113.63, 122.89, 123.87, 129.07, 131.79, 138.11, 158.39. Exact mass. Calcd for $C_{12}H_{14}O$: 174.1044. Found: 174.1091. **8**: Oil, bp 118-121 °C / 1 mmHg. ^{1}H NMR δ 1.87 (s, 3H), 2.19 (d, J = 8.1 Hz, 2H), 2.78 (d, J = 8.1 Hz, 2H), 3.76 (s, 3H), 6.15 (br s, 1H), 6.62-6.74 (m, 2H), 6.87 (d, J = 8.9 Hz, 1H). ^{13}C NMR δ 23.34, 28.54, 28.62, 55.21, 110.97, 113.53, 121.99, 125.91, 128.24, 135.35, 135.67, 157.96. Exact mass. Calcd for $C_{12}H_{14}O$: 174.1044. Found: 174.1024.

General Procedure of Photoamination. Into a Pyrex vessel was introduced an MeCN-H_2O (9:1, 70 mL) solution containing **1-4**, **6-8** (3.5 mmol) and DCB (3.5 mmol), and then the solution was bubbled with gaseous ammonia. The solution was irradiated by an Eikosha PIH-300 high-pressure mercury lamp under cooling with water. The progress of reaction was followed by GLC analysis. After evaporation of solvent, the photolysates were acetylated with Ac_2O and then chromatographed on silica gel. In the case of alkylamine, an MeCN (70

mL) solution containing **4-7** (3.5 mmol) and DCB (3.5 mmol) was bubbled with argon gas, and then an amine (17.5 mmol) was added to the solution. Photoreaction was performed in a similar way to the case of NH_3. After the evaporation of solvent, the photolysates were separated by column chromatography on silica gel.

2-Amino-1-(2-methoxyphenyl)propane (9a): The acetamide. Mp 92.5-93.0 °C (from hexane / benzene). ^{1}H NMR δ 1.15 (d, J = 6.6 Hz, 3H), 1.86 (s, 3H), 2.72 (dd, J = 13.5, 5.9 Hz, 1H), 2.81 (dd, J = 13.5, 7.6 Hz, 1H), 3.84 (s, 3H), 4.12-4.23 (m, 1H), 5.95 (br s, 1H), 6.85-6.98 (m, 2H), 7.10-7.24 (m, 2H). ^{13}C NMR δ 20.64, 23.47, 36.44, 46.62, 55.32, 110.45, 120.72, 126.76, 127.83, 131.18, 157.42, 169.43. Exact mass. Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1259.

2-Amino-1-(3-methoxyphenyl)propane (9b): The acetamide. Oil, ^{1}H NMR δ 1.07 (d, J = 6.7 Hz, 3H), 1.89 (s, 3H), 2.62 (dd, J = 13.4, 7.3 Hz, 1H), 2.78 (dd, J = 13.4, 5.8 Hz, 1H), 3.75 (s, 3H), 4.14-4.25 (m, 1H), 5.70 (br d, 1H), 6.69-6.74 (m, 3H), 7.14-7.20 (m, 1H). ^{13}C NMR δ 19.95, 23.42, 42.42, 46.11, 55.16, 111.77, 115.12, 121.82, 129.34, 139.59, 159.60, 169.56. Exact mass. Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1258.

2-Amino-1-(3,4-dimethoxyphenyl)propane (9c): The acetamide. Oil, ^{1}H NMR δ 1.11 (d, J = 6.6 Hz, 3H), 1.94 (s, 3H), 2.63 (dd, J = 13.6, 7.3 Hz, 1H), 2.80 (dd, J = 13.6, 5.6 Hz, 1H), 3.86 (s, 6H), 4.16-4.27 (m, 1H), 5.52 (br d, 1H), 6.69-6.82 (m, 3H). ^{13}C NMR δ 19.94, 23.48, 42.01, 46.21, 55.88, 55.88, 111.14, 112.53, 121.42, 132.27, 147.65, 148.83, 169.44. Exact mass. Calcd for $C_{13}H_{19}NO_3$: 237.1365. Found: 237.1364.

2-Amino-1-(4-methoxyphenyl)propane (9d): The acetamide. Oil, ^{1}H NMR δ 1.09 (d, J = 6.7 Hz, 3H), 1.93 (s, 3H), 2.63 (dd, J = 13.6, 7.2 Hz, 1H), 2.77 (dd, J = 13.6, 5.7 Hz, 1H), 3.78 (s, 3H), 4.14-4.25 (m, 1H), 5.74 (br d, 1H), 6.83 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 19.81, 23.29, 41.44, 46.40, 55.24, 113.85, 129.98, 130.38, 158.28, 170.01. Exact mass. Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1258.

2-Amino-1-(4-cyanophenyl)-1-(3,4-dimethoxyphenyl)propane (10c): The acetamide. Oil, ^{1}H NMR δ 1.12 (d, J = 6.4 Hz, 3H), 1.81 (s, 3H), 3.84 (s, 6H), 3.84-3.87 (m, 1H), 4.81-4.98 (m, 1H), 5.44 (br d, 1H), 6.69-6.72 (m, 2H), 6.80 (s, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 20.30, 23.34, 47.13, 55.86, 55.86, 58.04, 110.34, 110.94, 111.40, 118.84, 120.32, 128.74, 132.29, 133.41, 147.92, 148.19, 149.24, 169.33. Exact mass. Calcd for $C_{20}H_{22}N_2O_3$: 338.1625. Found: 338.1628.

2-Amino-1-(4-cyanophenyl)-1-(4-methoxyphenyl)propane (10d): A mixture of stereo isomers. Oil, ^{1}H NMR δ 1.10 (d, J = 6.4 Hz, 3H), 2.08 (s, 3H), 3.76 (s, 3H), 3.84-3.91 (m, 1H), 4.80-4.93 (m, 1H), 5.61 and 5.71 (br d, J = 9.0 and 9.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.36-7.43 (m, 2H), 7.52-7.57 (m, 2H). Major isomer: ^{13}C NMR δ 20.09, 23.17, 47.43, 55.24, 57.60, 110.19, 114.39, 118.87, 128.78, 129.13, 132.27, 132.94, 148.16, 158.70, 169.83. Minor isomer: ^{13}C NMR δ 20.44, 23.26, 47.12, 55.24, 57.08, 110.45, 114.24, 118.75, 128.92, 129.20, 132.39, 132.52, 148.33, 158.64, 169.94. Exact mass. Calcd for $C_{19}H_{20}N_2O_2$: 308.1520. Found: 308.1524.

1-(4-Cyanophenyl)-2-isopropylamino-1-(4-methoxyphenyl)propane (10e): Oil, ^{1}H NMR δ 0.96-1.02 (m, 9H), 2.63 (br s, 1H), 2.83-2.93 (m, 1H), 3.50-3.56 (m, 1H), 3.77 (s, 3H), 3.81 (d, J = 9.9 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H). ^{13}C NMR δ 18.85, 21.81, 24.29, 45.84, 52.86, 55.23, 58.32, 110.18, 114.46, 118.86, 129.06, 129.29, 132.34, 132.85, 149.20, 158.75. The acetamide. Exact mass. Calcd for $C_{22}H_{26}N_2O_2$: 350.1988. Found: 350.1993.

2-*t*-Butylamino-1-(4-cyanophenyl)-1-(4-methoxyphenyl)propane (10f): A mixture of stereo isomers. Oil, ^{1}H NMR δ 0.96 (s, 9H), 1.03 (d, J = 5.9 Hz, 3H), 3.47-3.58 (m, 1H), 3.70 (d, J = 9.6 Hz, 1H), 3.75 (s, 3H), 6.84 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H). Major isomer: ^{13}C NMR δ 22.64, 29.85, 50.42, 50.50, 54.86, 59.26, 109.59, 113.82, 118.69, 129.02, 129.34, 131.89, 132.92, 148.99, 158.30. Minor isomer: ^{13}C NMR δ 22.95, 28.99, 50.42, 50.74, 53.50, 59.63, 109.59, 113.71, 118.68, 128.02, 129.19, 131.69, 133.74, 149.14, 157.98. Exact mass. Calcd for $C_{21}H_{27}N_2O$: 323.2125. Found: 323.2097.

***trans*-1-(2-Isopropylamino-3,5-dimethoxyphenyl)propane (11)**: Oil, ^{1}H NMR δ 1.06 (d, J = 6.3 Hz, 6H), 1.90 (dd, J = 6.5, 1.5 Hz, 3H), 3.20 (sept, J = 6.3 Hz, 1H), 3.77 (s, 3H), 3.79 (s, 3H), 6.05-6.17 (m, 1H), 6.32 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 2.5 Hz, 1H), 6.64 (d, J = 15.8 Hz, 1H). ^{13}C NMR δ 18.73, 23.35, 50.29, 55.22, 55.55, 97.52, 101.51, 125.07, 128.76, 131.54, 132.69, 153.38, 154.83. The acetamide. Exact mass. Calcd for $C_{16}H_{23}NO_3$: 277.1676. Found 277.1667.

2-Amino-6-methoxy-1,2,3,4-tetrahydronaphthalene (12a): The acetamide. Mp 106.0-108.0 °C (from benzene / hexane), ^{1}H NMR δ 1.68-1.82 (m, 1H), 1.88-2.09 (m, 1H), 1.96 (s, 3H), 2.56 (dd, J = 16.0, 8.0 Hz, 1H), 2.77-2.88 (m, 2H), 3.03 (dd, J = 16.0, 5.1 Hz, 1H), 3.77 (s, 3H), 4.22-4.28 (m, 1H), 5.78 (br d, 1H), 6.63 (br s, 1H), 6.69 (dd, J = 8.3, 2.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H). ^{13}C NMR δ 23.50, 27.29, 28.45, 34.81, 45.31, 55.23, 112.34, 113.32, 126.03, 130.33, 136.60, 157.90, 169.70. Exact mass. Calcd for $C_{13}H_{17}NO_2$: 219.1258. Found: 219.1172.

2-Amino-6-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (12d): A mixture of trans and cis isomers. The acetamide. Mp 130.0-135.0 °C (from benzene / hexane). Major isomer: ^{1}H NMR δ 1.28 (d, J = 7.1 Hz, 3H), 1.79-2.11 (m, 2H), 2.70-2.89 (m, 2H), 1.95 (s, 3H), 3.07-3.17 (m, 1H), 3.78 (s, 3H), 4.03-4.08 (m, 1H), 5.66 (br d, 1H), 6.62 (br s, 1H), 6.72-6.77 (m, 1H), 7.08 (d, J = 8.5 Hz, 1H). ^{13}C NMR δ 22.11, 23.55, 24.24, 25.97, 38.15, 50.33, 55.19, 112.71, 113.19, 130.19, 131.19, 136.29, 157.71, 169.69. Minor isomer: ^{1}H NMR δ 1.20 (d, J = 7.0 Hz, 3H), 1.79-2.11 (m, 2H), 1.98 (s, 3H), 2.70-2.89 (m, 2H), 2.92-3.02 (m, 1H), 3.78 (s, 3H), 4.29-4.37 (m, 1H), 5.58 (br d, 1H), 6.62 (br s, 1H), 6.72-6.77 (m, 1H), 7.08 (d, J = 8.5 Hz, 1H). ^{13}C NMR δ 17.17, 23.51, 25.17, 27.28, 34.93, 48.84, 55.19, 112.41, 113.14, 129.47, 131.89, 136.22, 157.78, 169.81. Exact mass. Calcd for $C_{14}H_{19}NO_2$: 233.1415. Found: 233.1420.

2-Amino-6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene (12g): The acetamide. Mp 100.0-101.0°C (from benzene / hexane), ^{1}H NMR δ 1.49 (s, 3H), 1.60-1.71 (m, 2H), 1.87 (s, 3H), 2.50-2.60 (m, 1H), 2.70-2.81 (m, 3H), 3.77 (s, 3H), 5.35 (br s, 1H), 6.65 (br s, 1H), 6.69 (dd, J = 8.3, 2.6 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H). ^{13}C NMR δ 24.36, 25.38, 26.35, 31.69, 41.82, 52.50, 55.21, 112.28, 113.33, 125.61, 130.43, 136.85, 157.93, 170.18. Exact mass. Calcd for $C_{14}H_{19}NO_2$: 233.1414. Found: 233.1413.

2-Amino-1-(4-cyanophenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene (13a): Oil, ^{1}H NMR δ 1.76-2.00 (m, 2H), 1.90 (br s, 2H), 2.88-3.02 (m, 2H), 3.15-3.21 (m, 1H), 3.76 (s, 3H), 3.84 (d, J = 10.0 Hz, 1H), 6.51 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 8.6 Hz, 1H), 6.67 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H). ^{13}C NMR δ 28.28, 30.68, 54.64, 55.21, 55.27, 110.56, 112.60, 113.15, 118.89, 129.31, 130.22, 131.10, 132.35, 137.61, 150.71, 158.09. Exact mass. Calcd for $C_{18}H_{18}N_2O$: 274.1105. Found: 274.1102.

2-Isopropylamino-1-(4-cyanophenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene (13b): A mixture of trans and cis isomers. Oil, *trans*-**13b**: ^{1}H NMR δ 0.86 (d, J = 6.1 Hz, 3H), 1.04 (d, J = 6.3 Hz, 3H), 1.62-1.76 (m, 1H), 1.93 (br s, 1H), 1.97-2.05 (m, 1H), 2.80-2.93 (m, 3H), 3.00-3.10 (m, 1H), 3.67 (s, 3H), 3.99 (d, J = 6.9 Hz, 1H), 6.57-6.68 (m, 3H), 7.22 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 22.54, 23.98, 26.08, 27.15, 44.95, 51.91, 55.22, 57.34, 110.27, 112.74, 113.20, 118.95, 128.76, 130.04, 131.67, 132.16, 137.85, 151.29, 158.14. Exact mass. Calcd for $C_{21}H_{24}N_2O$: 320.1886: Found: 320.1879. *cis*-**13b:** ^{1}H NMR δ 1.11 (d, J = 6.0 Hz, 3H), 1.03 (d, J = 5.7 Hz, 3H), 1.40 (br s, 1H), 1.48-1.62 (m, 1H), 1.75-1.83 (m, 1H), 2.96-3.12 (m, 2H), 3.19-3.28 (m, 2H), 3.79 (s, 3H), 4.33 (d, J = 5.0 Hz, 1H), 6.61-6.71 (m , 3H), 7.15 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H). ^{13}C NMR δ 23.16, 23.26, 24.95, 28.96, 44.95, 48.58, 53.71, 55.22, 110.08, 112.80, 113.09, 119.04, 129.84, 131.32, 131.32, 131.52, 137.76, 148.22, 158.38.

2-*t*-Butylamino-1-(4-cyanophenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene (13c): Mp 138.0-140.0 °C (from benzene / hexane), ^{1}H NMR δ 0.87 (s, 9H), 1.57-1.72 (m, 1H), 2.04-2.16 (m, 1H), 2.85-3.01 (m, 3H), 3.77 (s, 3H), 3.79 (d, J = 10.3 Hz, 1H), 6.54-6.63 (m, 2H), 6.67 (br s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 28.33, 29.88, 31.17, 50.84, 54.18, 55.19, 55.37, 110.20, 112.51, 112.94, 119.00, 129.78, 130.45, 131.70, 131.99, 138.24, 151.71, 157.95. Exact mass. Calcd for $C_{22}H_{26}N_2O$: 334.2047. Found: 334.2075.

2-Amino-1-(4-cyanophenyl)-1-methyl-1,2,3,4-tetrahydronaphthalene (13d): The acetamide. Oil, ^{1}H NMR δ 1.68 (s, 3H), 1.71-1.83 (m, 2H), 1.93 (s, 3H), 2.88 (t, J = 6.8 Hz, 2H), 3.82 (s, 3H), 4.62-4.70 (m, 1H), 5.61 (br d, 1H), 6.72 (d, J = 2.6 Hz, 1H), 6.78 (dd, J = 8.6, 2.7 Hz, 1H), 6.96 (d, J = 8.6 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 23.43, 23.98, 25.20, 26.02, 46.52, 53.94, 55.21, 109.94, 113.34, 118.88, 128.30, 130.15, 131.85, 132.36, 136.92, 154.76, 158.31, 169.75. Exact mass. Calcd for $C_{21}H_{22}N_2O_2$: 334.1680. Found: 334.1694.

1-(4-Cyanophenyl)-2-isopropylamino-1-methyl-1,2,3,4-tetrahydronaphthalene (13e): Mp 121.0-121.5 °C (from benzene / hexane), ^{1}H NMR δ 0.52 (d, J = 6.1 Hz, 3H), 0.92 (d, J = 6.2 Hz, 3H), 1.58 (s, 3H), 1.69-1.86 (m, 1H), 1.88-2.00 (m, 1H), 2.47-2.63 (m, 1H), 2.87-2.99 (m, 3H), 3.74 (s, 3H), 6.53-6.63 (m, 3H), 7.33 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H). ^{13}C NMR δ 21.99, 22.65, 23.98, 25.47, 29.15, 46.26, 48.20, 54.77, 61.84, 109.08, 112.46, 118.81, 128.00, 130.67, 130.98, 136.52, 136.72, 155.97, 157.33. Exact mass. Calcd for $C_{22}H_{26}N_2O$: 334.2043. Found: 334.2006.

2-*t*-Butylamino-1-(4-cyanophenyl)-1-methyl-1,2,3,4-tetrahydronaphthalene (13f): Mp 110.5-111.0 °C (from benzene / hexane), ^{1}H NMR δ 0.67 (s, 9H), 1.56 (s, 3H), 1.81-1.99 (m, 2H), 2.85-2.91 (m, 2H), 2.97-3.04 (m, 1H), 3.77 (s, 3H), 6.50-6.62 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H). ^{13}C NMR δ 22.84, 29.37, 29.66, 30.07, 49.24, 50.48, 55.13, 58.90, 109.24, 112.52, 112.66, 119.27, 129.69, 131.14, 131.41, 136.99, 137.59, 156.61, 157.51. Anal. Calcd for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.10; N, 8.04 %. Found: C, 79.00; H, 8.23; N, 7.77 %.

2-Amino-1-(4-cyanophenyl)-2-methyl-1,2,3,4-tetrahydronaphthalene (13g): The acetamide. ^{1}H NMR δ 1.31 (s, 3H), 1.72-2.02 (m, 2H), 1.92 (s, 3H), 2.87-3.17 (s, 2H), 3.78 (s, 3H), 4.08 (s, 1H), 4.76 (br s, 1H), 6.62-6.68 (m, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H). ^{13}C NMR δ 22.45, 26.48, 26.61, 31.89, 52.52, 55.22, 58.21, 110.77, 113.03, 113.16, 118.78, 128.68, 131.47, 131.74, 131.86, 135.95, 147.37, 158.36, 176.55. Exact mass. Calcd for $C_{21}H_{22}N_2O_2$: 334.1680. Found: 334.1642.

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