HETEROCYCLES, Vol. 57, No. 2, 2002, pp. 269-292, Received, 15th November, 2001

AN EFFICIENT TRANSFORMATION OF SUBSTITUTED *N*-ACYL-α-DEHYDRO(1-NAPHTHYL)ALANINES INTO 1,2-DIHYDROBENZO[*f*]QUINOLINONE DERIVATIVES *VIA* PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER

Toyohisa Motohashi, Kei Maekawa, Kanji Kubo,† Tetsutaro Igarashi, and Tadamitsu Sakurai*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221-8686, Japan

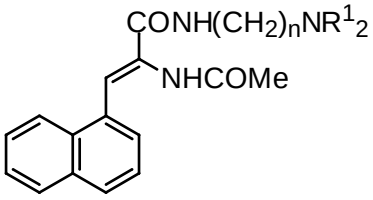
†Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

Abstract–The irradiation of substituted (*Z*)-*N*-acyl-α-dehydro(1-naphthyl)alanines (**1**) having the dialkylamino donor on the carboxamide side chain in methanol was found to give 1,2-dihydrobenzo[*f*]quinolinone derivatives (**2**) in good yields, which were formed *via* the electron-transfer reaction in the excited-state (*E*)-isomers, while intramolecular photocyclization reactions in the (*Z*)- and (*E*)-isomers afforded minor amounts of benzo[*f*]isoquinolines (**3**) and 1-azetines (**4**), respectively. The replacement of the *N*-acetyl group by the benzoyl (having stronger electron-withdrawing ability and larger steric bulkiness than the former) increased the selectivity for **2** and **4**, and this increased selectivity was mainly reflected in a great lowering of that for **3**.

INTRODUCTION

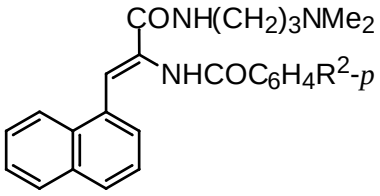
Photochemistry has continued to contribute to the development of efficient and selective transformations of organic materials into pharmaceutically important heterocyclic compounds. In recent years much attention has been devoted to the synthetic application of excited-state processes initiated by electron transfer, owing to the fact that many photoinduced electron-transfer (PET) reactions proceed in high chemical and quantum yields enabling the construction of biologically active heteroatom-containing polycyclic compounds.[1,2] In contrast to PET reactions of aromatic olefins,[2] there is no systematic study regarding the reactions of α,β-unsaturated α-amino acid (α-dehydroamino acid) derivatives. Taking into account the facts that efficient synthetic routes to α-dehydroamino acid derivatives have been developed but there has been only a limited investigation of the photochemistry of these amino acid derivatives,[3,4] we embarked on a

systematic study toward the characterization of the excited-state behavior of substituted α-dehydroamino acids including their PET reactions.[5,6] In the course of this study we discovered interesting photocyclizations of substituted α-dehydrophenylalanines affording isoquinoline and 1-azetine derivatives,[5] as well as novel intermolecular ET-initiated cyclization reactions in the α-dehydronaphthylalanine-triethylamine systems giving 1,2-dihydrobenzo[*f*]quinolinone derivatives.[6] Because α-dehydroamino acids and α-dehydropeptides possess a variety of biological activities,[7] these findings allow us to expect the potential pharmacological and physiological activities of isoquinoline and dihydrobenzoquinolinone derivatives obtained. It is, thus, significant extention to examine the synthetic utility of intramolecular ET-initiated photocyclizations of α-dehydronaphthylalanines, which may enable the introduction of the *N*,*N*-dialkylaminoalkyl group into the quinolinone skeleton. For this purpose, we designed (*Z*)-*N*-acyl-α-dehydro(1-naphthyl)alanines having dialkylamino electron donors (**1a**–**j**)[8] and investigated substituent effects on both the photoreactivity of **1** and the selectivity of each photoproduct, hoping to develop a new synthetic route to 1,2-dihydrobenzoquinolinones bearing a *N*,*N*-dialkylaminoalkyl substituent and also to shed some light on their formation mechanism.



(*Z*)-**1a**–**d**

1a (n= 3, R^1= Me)
1b (n= 3, R^1= Et)
1c (n= 3, R^1= Pr)
1d (n= 2, R^1= Me)



(*Z*)-**1e**–**j**

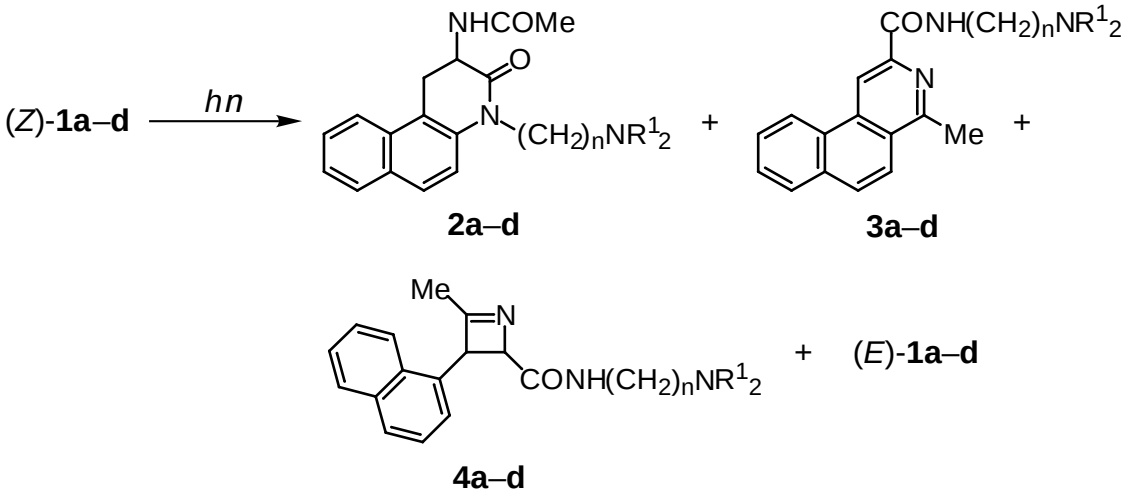
1e (R^2= OMe) **1f** (R^2= Me)
1g (R^2= H) **1h** (R^2= Cl)
1i (R^2= CF_3) **1j** (R^2= CN)

RESULTS AND DISCUSSION

(*Z*)-*N*-Acetyl-α-dehydro(1-naphthyl)alanine derivatives [(*Z*)-1a–d]

The starting (*Z*)-isomers (**1a**–**d** and **1e**–**j**) were prepared by the ring-opening reactions of the corresponding 1-naphthyl-substituted oxazolone with *N*,*N*-dialkylaminoalkylamines in good yields.[9] After a nitrogen-purged methanol solution of (*Z*)-**1a** (5.0×10^{-3} mol dm^{-3}) was irradiated with Pyrex-filtered light (>280 nm) from a 400 W high-pressure Hg lamp for 120 min at room temperature, the crystalline product mixtures obtained were washed first with small amounts of dry ether and then with hexane, giving analytically pure 1,2-dihydrobenzo[*f*]quinolinone derivative (**2a**) in 60% yield, the structure of which was determined by its 2D NMR (^{1}H–^{1}H and ^{1}H–^{13}C COSY) spectra. Preparative TLC (silica gel) of the residual solid [that was obtained by evaporating the filtrate (ether–hexane) to dryness] enabled isolation of substituted benzo[*f*]isoquinoline (**3a**; <5%). In addition, we succeeded in isolating the (*E*)-isomer from the reaction mixture obtained by the 15 min irradiation of (*Z*)-**1a**. Careful ^{1}H NMR spectral analysis of the product mixture suggested that there was very little formation of the *cis*-azetine isomer (**4a**) whose

ring-proton signals with the $J_{3,4}$ value of 10.7 Hz were detected at 5.06 and 6.53 ppm,[5a–c] though attempts to isolate **4a** from the mixture were unsuccessful owing to its poor yield (Scheme 1).



Scheme 1

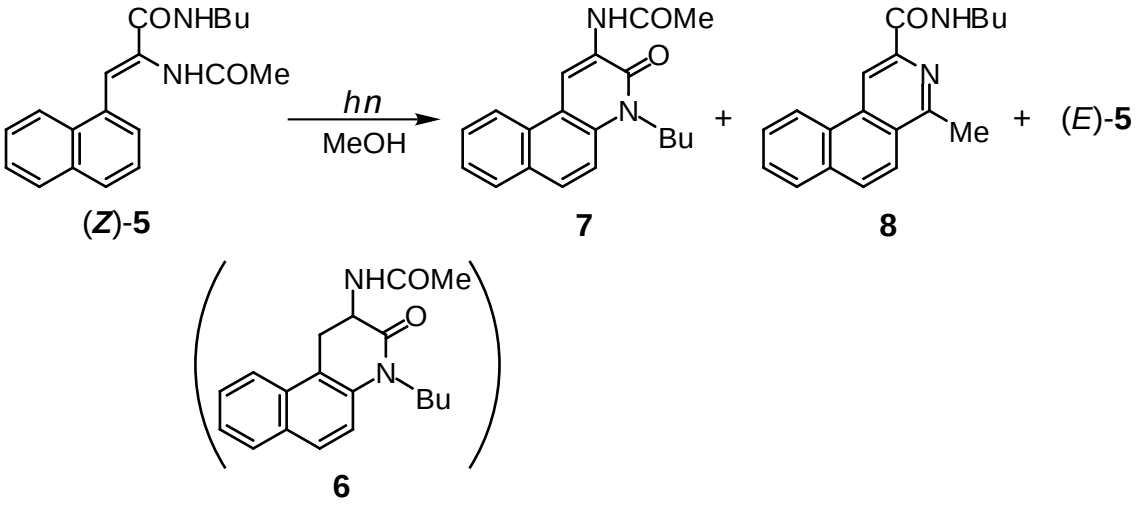
In a previous study it was found that the rapid $Z \rightarrow E$ isomerization of substituted *N*-acetyl-α-dehydro(1-naphthyl)alanines occurs prior to the appearance of the photoproducts and, additionally, induces a relatively large downfield shift of the *N*-acetylamide proton signal.[6] Thus, taking into account the fact that the *N*-acetylamide proton of (*Z*)-**1a** exhibits its singlet peak at 9.25 ppm, the 9.71 ppm signal is definitely assigned to the amide proton of (*E*)-**1a**. The finding that the photoproducts (**2a**–**4a**) are stable enough such that they undergo only negligible decomposition under the irradiation conditions used allowed us to monitor the reactions by means of ^{1}H NMR spectroscopy, as shown in Table 1. The results in Table 1 demonstrate the rapid production of (*E*)-**1a** and the subsequent increase in compositions for **2a**–**4a** with the decrease of the isomer compositions, being consistent with the mechanism in which the excited-state (*E*)- and (*Z*)-isomers serve as precursors of these products.

Table 1. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**1a** in methanol

Compound	Irradiation time /min						
	0	15	30	45	60	90	120
(Z)-**1a**	100	39.0	27.4	18.7	11.8	3.2	0.0
(E)-**1a**	0	40.5	31.6	21.8	15.1	4.9	1.5
2a	0	14.8	31.6	46.2	58.9	74.9	78.5
3a	0	5.1	8.2	11.4	12.1	14.3	17.6
cis-**4a**	0	0.5	1.2	1.7	2.1	2.7	2.4

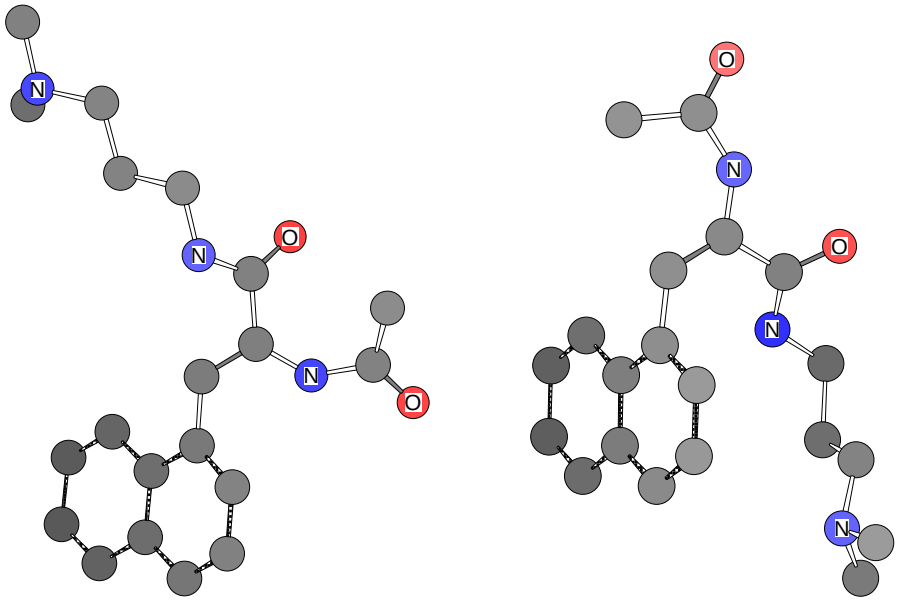
On the other hand, there was no formation of the dihydrobenzoquinolinone derivative (**6**) when a nitrogen-purged MeOH solution of (*Z*)-**5** (6.6×10^{-3} mol dm^{-3}) was irradiated with Pyrex-filtered light from a 450 W

high-pressure Hg lamp for 40 h (^{1}H NMR spectral analysis), suggesting that ET from the dimethylamino nitrogen to the excited-state naphthylmethylene moiety in **1a** participates in the appearance of **2a** as the primary process. Instead, the benzo[*f*]quinolinone derivative (**7**) was isolated as major product (22%) along with the benzo[*f*]isoquinoline derivative (**8**, 15%), (*E*)-**5** (14%), and (*Z*)-**5** (10%) (Scheme 2). A ^{1}H NMR spectral analysis of the product mixture revealed that the presence of unknown



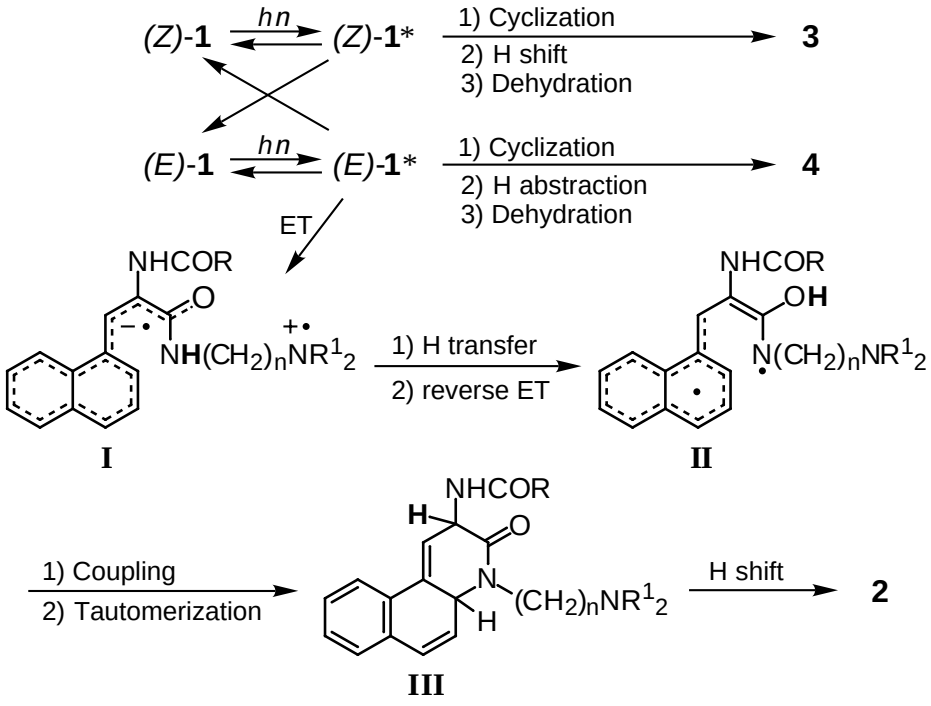
Scheme 2

products makes it very difficult to detect proton signals attributable to the corresponding 1-azetine derivative. The structure of **7** was established by measurements of its physical and spectroscopic parameters, as well as of its 2D NOESY spectrum in which strong correlation was observed between the ring proton at the 5-position (the signal of which appears at 7.54 ppm) and the protons of the butyl methylene group (giving their signal at 4.50 ppm) attached to the ring nitrogen. Although it is suggested that molecular oxygen incorporated into gaseous nitrogen as a contaminant is involved in the dehydrogenation of an intermediate (formed *via* the excited-state (*E*)-isomer) to eventually afford **7**, the fact that molecular oxygen affects the reaction to only a negligible extent requires further studies for elucidating the formation mechanism of this quinolinone derivative. In addition to these findings, the occurrence of intramolecular fluorescence quenching in (*Z*)-**1a** (5.0×10^{-5} mol dm^{-3}; emission-intensity ratio of **5** to **1a** at 376 nm= 1.4 in nitrogen-saturated methanol; excitation wavelength, 280 nm) confirms that ET from the dimethylamino nitrogen to the excited-state naphthylmethylene moiety participates in the appearance of **2a** as the primary process. The occurrence of intramolecular ET is supported also by the observation that an increase in the concentration of the starting (*Z*)-**1a** ($5.0 \times 10^{-5} \rightarrow 5.0 \times 10^{-3}$ mol dm^{-3}) influences the product composition at a given conversion of the starting **1a** to only a slight extent (UV and ^{1}H NMR spectral analyses). MM2 calculations for the ground-state conformations of (*Z*)-**1a** and (*E*)-**1a** indicate that the (*E*)-isomer adopts a most suitable conformation for "through-space" ET (Figure 1). Accordingly, these considerations led us to propose Scheme 3 in which intramolecular ET from the dimethylamino nitrogen to the naphthylmethylene moiety in the excited singlet-state (*E*)-isomer forms the radical ion pair intermediate (**I**), in competition with the intramolecular cyclization of this isomer eventually giving the 1- azetine derivative (**4**). Hydrogen



(*Z*)-**1a** (*E*)-**1a**

Figure 1. Energy-minimized conformations of (*Z*)-**1a** and (*E*)-**1a**



R= Me; R^1= Me, Et, Pr; n= 2, 3

Scheme 3

transfer from the amide nitrogen to the amide carbonyl oxygen within the intermediate (**I**) and the subsequent reverse ET to the dimethylamino radical cation affords the enol-type biradical intermediate (**II**), the coupling and tautomerization of which generate the cyclization product (**III**). The process that reaches the dihydrobenzoquinolinone derivative (**2**) is completed by aromatization of **III** *via* hydrogen shift.

According to Scheme 3, we predict that the *N*-aminoalkylamide hydrogen in the starting **1** should migrate to the 2-position of the benzoquinolinone ring upon forming **2**. After the H-D exchange reaction for the amide protons of (*Z*)-**1a** (5.0×10^{-3} mol dm^{-3}) in MeOD was completed (12 h incubation), deuteriated **1a** was irradiated for 120 min in the same solvent under similar conditions. The ^{1}H NMR spectrum of the reaction mixture in DMSO-d_6, obtained after usual work-up, clearly showed disappearance of the 4.58 ppm signal that had been ascribed to the proton attached to the 2-position in the ring. The above result is consistent with our prediction, thereby substantiating the mechanism proposed for the formation of **2**.

Table 2. Substituent effects on the photoreactivity and product composition of the starting *(Z)*-**1** in methanol

Compound	Irradiation time /min	Composition (%)				
		(Z)-**1**	*(E)*-**1**	**2**	**3**	*cis*-**4**
1a	15	39.0	40.5	14.8	5.1	0.5
	120	0.0	1.5	78.5	17.6	2.4
1b	15	46.8	36.0	14.6	2.0	0.7
	120	5.9	0.8	83.8	5.9	3.6
1c	15	39.6	37.3	20.5	2.0	0.6
	120	0.0	0.0	92.2	5.1	2.7
1d	15	41.3	39.6	12.5	5.8	0.8
	120	1.2	1.1	75.0	19.7	3.0

In order to shed some light on the mechanism of ET-induced photocyclization reactions of (*Z*)-**1** and the scope of these reactions in the synthesis of substituted 1,2-dihydrobenzo[*f*]quinolinones (**2**), we investigated substituent effects on the photoreactivity and product composition of (*Z*)-**1** in methanol. The results obtained are collected in Table 2 which clearly shows that both the alkyl substituent R^1 and the methylene-chain length (n) exert only small effects on the reactivity of the excited-state (*Z*)-isomer and its isomerization efficiency. Because both the (*Z*)- and (*E*)-isomers are consumed completely by much longer irradiation, we may define a selectivity for the dihydrobenzoquinolinone derivative (**2**) as the ratio of composition for this derivative to the sum of product composition, namely, **2**/(**2** + **3** + **4**) which is independent of irradiation time. The selectivity of each product thus defined was estimated by employing the compositions obtained at three different irradiation times (60, 90 and 120 min) and its average value is summarized in Figure 2. Interestingly, the selectivities of **2** and **4** have a tendency to increase with an increase in electron-donating ability of the substituent R^1: Me (**2a**, **4a**)< Et (**2b**, **4b**)< Pr (**2c**, **4c**), although a clear tendency is not observed for the latter selectivity owing to its rather small value. An increase in the former selectivity is mainly reflected in a lowering of the selectivity for substituted benzoisoquinolines (**3**), being consistent with the mechanism in which ET to the excited-state (*E*)-**1** occurs in competition with the isomerization into (*Z*)-**1** whose photocyclization eventually gives **3**, as shown in Scheme 3. The finding that ET process forming the radical ion pair intermediate (**I**) is not subject to the large steric hindrance of the

substituent R^1 allows us to propose a "through-space" ET mechanism in which the 1-naphthylmethylene acceptor and the dialkylamino donor are not required to come into contact. As seen from Figure 2, there is only a small difference in the selectivity of each product between **1a** (R= Me; R^1= Me; n= 3, Scheme 3) and **1d** (R= Me; R^1= Me; n= 2), suggesting the minor effect of the methylene-chain length (n) on the ET efficiency if we consider the experimental error allowed for our selectivity estimation. Thus, this observation substantiates the proposal described above.

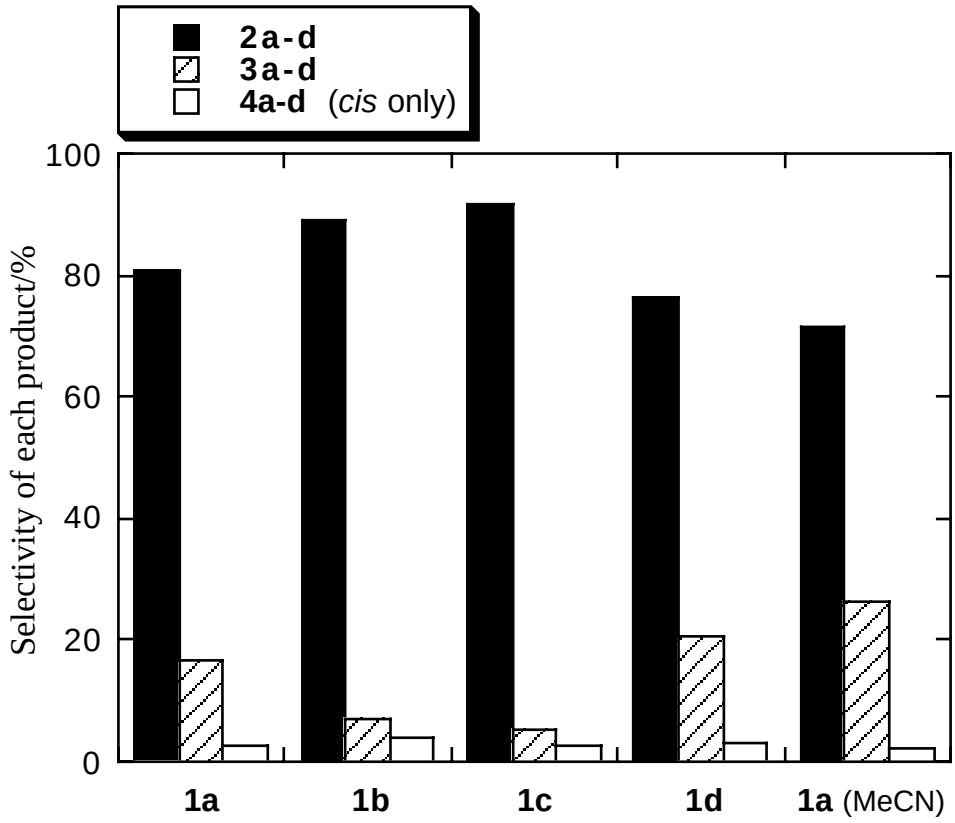


Figure 2. Substituent and solvent effects on the selectivity of each product obtained by the irradiation of (*Z*)-**1** in methanol

It was previously shown that ET from the tertiary amino nitrogen takes place more efficiently in acetonitrile than in methanol because of the formation of hydrogen bonding in the latter solvent.[8,10] Thus, we may expect the enhancement of both the photoreactivity of (*Z*)-**1** and the selectivity of the dihydrobenzoquinolinone derivative (**2**) in the former solvent. In Table 3 are shown compositions of **1a**–**4a** obtained by the irradiation of (*Z*)-**1a** (5.0×10^{-3} mol dm^{-3}) in acetonitrile under the same conditions. A comparison of the data shown in Tables 1 and 3 reveals that the excited-state reactivities of both isomers are much higher in the protic polar solvent, methanol, than in the aprotic polar solvent, acetonitrile, being not consistent with our expectation. Additionally, the latter solvent lowers not only the relative rate for the *Z*→*E* isomerization (15 min irradiation) but also the selectivity of **2a** (80.6 → 71.4% at 120 min irradiation, Figure 2). These observations cannot be explained in terms of the disappearance of hydrogen-bonding solvation of the dimethylamino nitrogen in acetonitrile. The fact that the amide carbonyl oxygen readily forms a hydrogen bond to a protic solvent molecule forces us to consider the hydrogen-bonding solvation

of the starting α-dehydronaphthylalanine derivatives in methanol,[11] because methanol (relative permittivity at 25 ℃, ε_{25}= 32.66) and acetonitrile (ε_{25}= 35.94) have almost the same polarity.[12] It is, thus, very likely that the solvation of the excited singlet-state (**1a**) by methanol accelerates the *Z*→*E* isomerization and then greatly enhances the electron-accepting ability of the naphthylmethylene moiety. The extent of the increase in this ability must be much larger, as compared to that of the decrease in electron-donating ability of the dimethylamino nitrogen in an **1a** molecule by hydrogen-bonding solvation.

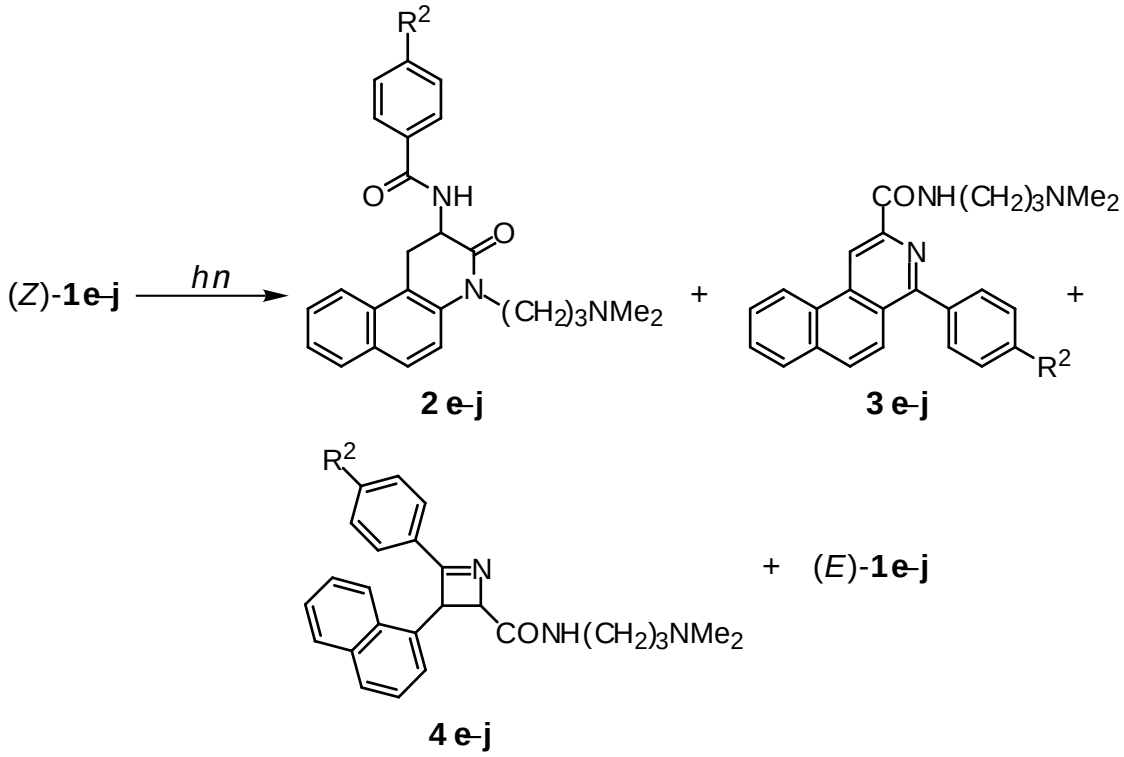
Table 3. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**1a** in acetonitrile

Compound	Irradiation time /min						
	0	15	30	45	60	90	120
(Z)-**1a**	100	76.7	66.6	58.6	51.9	36.6	25.6
(E)-**1a**	0	16.1	16.1	16.5	16.6	17.6	18.6
2a	0	4.5	11.9	17.4	22.2	32.7	40.3
3a	0	2.4	4.8	6.9	8.5	12.0	14.2
cis-**4a**	0	0.3	0.6	0.6	0.7	1.1	1.3

(*Z*)-*N*-(*p*-Substituted benzoyl)-α-dehydro(1-naphthyl)alanine derivatives [(*Z*)-1e–j]

It was previously found that the intramolecular cyclization of the excited-state (*Z*)-*N*-benzoyl-α-dehydrophenylalanines is completely suppressed (owing to steric effects of the bulky benzoyl group) to give selectively 1-azetines *via* the (*E*)-isomer without forming any isoquinolines.[5b,c] If we consider relatively strong electron-accepting abilities of the 1-naphthylmethylene and benzoyl groups (in addition to this finding), we are allowed to predict that the introduction of the benzoyl group (instead of the acetyl) into (*Z*)-**1** would increase compositions for **2** and **4** by inhibiting the formation of the benzoisoquinoline derivative (**3**) (Scheme 4). According to the procedure that was applied to (*Z*)-**1a**–**d**, a nitrogen-purged methanol solution of (*Z*)-**1g** (R^2= H, 5.0×10^{-3} mol dm^{-3}) was irradiated with Pyrex-filtered light at room temperature, and at suitable time intervals the reaction mixture was subjected to ^{1}H NMR spectral analysis in order to estimate the composition of each compound (Table 4). By comparing the data shown in Tables 1 and 4, one can see that the overall reactivity of the excited-state (**1g**) is decreased to some extent and also the presence of the *N*-benzoyl group lowers the relative rate for the isomerization into the (*E*)-isomer (15 min irradiation). In addition, we observed the enhanced compositions of substituted dihydrobenzoquinolinone (**2a**) and 1-azetine (**4a**) whereas there was a substantial decrease in composition for **3a** (120 min irradiation), being consistent with our prediction. As described above, the *N*-benzoyl substituent in (*Z*)-**1g** possesses a stronger electron-accepting power [as compared to the *N*-acetyl in (*Z*)-**1a**] and also exhibits its UV absorption around 280 nm, so that a charge transfer (CT)-type interaction between the dimethylamino nitrogen and the benzoyl moiety in the excited singlet state makes it possible to deactivate the (*Z*)-isomer more greatly than the (*E*)-isomer (Figure 3).

In order to obtain a piece of evidence for the CT-type interaction, we investigated substituent (R^2) effects on



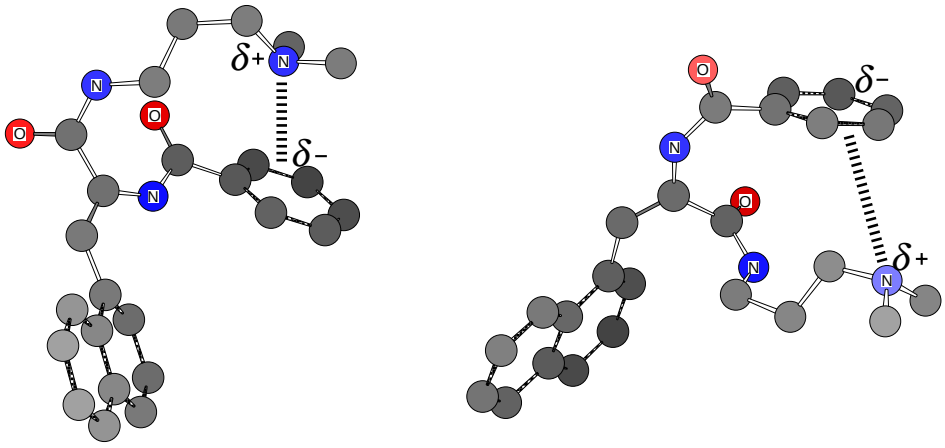
Scheme 4

Table 4. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**1g** in methanol

Compound	Irradiation time /min						
	0	15	30	45	60	90	120
(Z)-**1g**	100	59.1	47.4	30.0	26.5	5.0	2.0
(E)-**1g**	0	26.6	24.0	17.8	14.0	2.9	2.1
2g	0	11.9	24.5	44.6	51.4	82.0	84.5
3g	0	0.3	0.5	0.7	0.8	1.2	1.4
cis-**4g**	0	1.8	3.2	6.1	6.5	7.9	8.5
trans-**4g**	0	0.2	0.4	0.8	0.8	1.0	1.5

the photoreactivity and product composition of (*Z*)-**1** while keeping the steric bulkiness of aromatic acyl groups constant (Scheme 4), and the results obtained are collected in Table 5. An inspection of Table 5 demonstrates that the reactivities of the excited-state (**1**) having aromatic acyl substituents have a clear propensity to decrease with increasing the electron-withdrawing ability of the substituent R^2: **1e** (R^2= OMe)≈ **1f** (Me) ≈ **1g** (H)> **1h** (Cl)> **1i** (CF_3)> **1j** (CN). In other words, there is a tendency for the (*Z*)-isomer composition to increase and for the (*E*)-isomer to decrease in nearly this order, when compared at the early stage of the reaction (15 min irradiation). Accordingly, the concept of the CT-type interaction between the dimethylamino nitrogen and the benzoyl moiety is substantiated by the observation of a considerable reduction of both the photoreactivity and the relative rate for the isomerization of (*Z*)-**1** bearing

a strong electron-withdrawing CN group.



(*Z*)-**1g** (*E*)-**1g**

Figure 3. Schematic illustration for a charge transfer-type interaction in (*Z*)-**1g** and (*E*)-**1g**

Table 5. Substituent effects on the photoreactivity and product composition of the starting *(Z)*-**1** in methanol

Compound	Irradiation time /min	Composition (%)				
		(Z)-**1**	*(E)*-**1**	**2**	**3**	**4**[a]
1e	15	55.6	22.8	19.2	1.4	1.0
	120	3.2	1.8	86.5	3.2	5.2
1f	15	55.5	25.6	15.6	1.2	2.1
	120	2.2	1.3	86.2	2.2	8.1
1g	15	59.1	26.6	11.9	0.3	2.0
	120	2.0	2.1	84.5	1.4	10.0
1h	15	63.5	24.5	9.8	0.0	2.2
	120	15.6	8.7	64.1	0.7	10.9
1i	15	81.1	15.7	2.1	0.0	1.1
	120	34.5	16.6	37.4	0.0	11.4
1j	15	94.3	3.9	0.7	0.0	1.1
	120	71.1	17.6	5.8	0.0	5.4

[a] The sum of *cis*- and *trans*-isomers.

Taking into account that the CT-type interaction [that contributes to the deactivation of the excited-state (*Z*)- and (*E*)-isomers] may affect selectivities of the products (**2**–**4**), we estimated these selectivities in the same manner as that described in the preceding section, and the selectivity data are summarized in Figure 4. Clearly, the increased electron-withdrawing ability of the substituent R^2 lowers not only the selectivity for dihydrobenzoquinolinones (**2**) but also for benzoisoquinolines (**3**). In contrast to **2** and **3**, 1-azetines

(**4**) show an inverse tendency and then the decrease in the selectivity of **2** is comparable to the increase in that of **4**. As already suggested, an increase in the contribution of the CT-type interaction in the excited-state (*Z*)-isomer should accelerate the deactivation of this isomer to result in a further decrease in the relative rate for the cyclization reaction that yields the isoquinoline derivative (**3**), being consistent with the results obtained and, hence, providing a good explanation for substituent effects on the selectivity of **3**. If there exists the CT-type interaction also in the excited-state (*E*)-isomer as shown in Figure 3, the rate of ET to this isomer (relative to the intramolecular cyclization process eventually giving **4**) is considered to decrease as the electron-withdrawing ability of R^2 is increased. Substituent effects on the selectivities of both **2** and **4**, therefore, present a strong piece of evidence for the mechanism shown in Scheme 3 [R= $C_6H_4R^2$-*p* (R^2= OMe, Me, H, Cl, CF_3, CN); R^1= Me; n= 3] and also for the presence of the CT-type interaction in an excited-state (*E*)-isomer molecule.

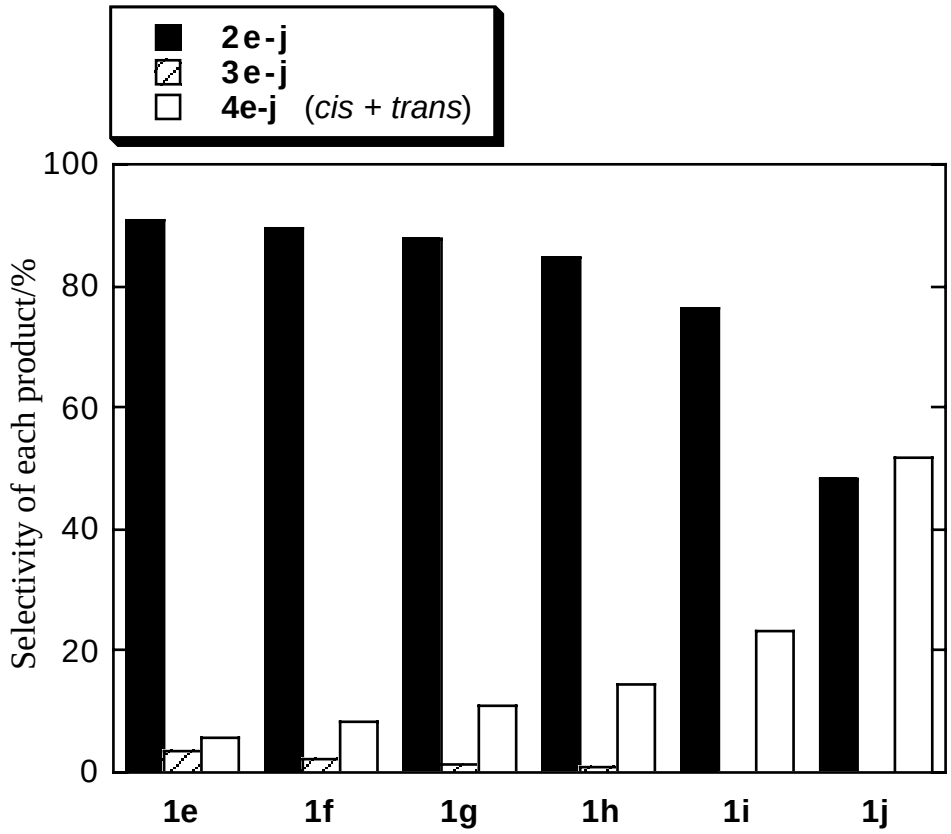


Figure 4. Substituent effects on the selectivity of each product obtained by the irradiation of (*Z*)-**1** in methanol

CONCLUSION

Although there are many synthetic routes to medium-sized lactams fused to an aromatic ring,[13] convenient photochemical routes to substituted dihydrobenzoquinolinones are scarcely known.[14] The procedure for preparing the starting **1** is very simple and is easily applicable to its related compounds. Taking into consideration the fact that the dihydrobenzoquinolinone derivatives (**2**) obtained in high yields are photochemically very stable, we were led to conclude that the intramolecular PET reaction of substituted *N*-acyl-α-dehydro(1-naphthyl)alanines (**1**) in methanol constitutes a novel photochemical method for

constructing the 1,2-dihydrobenzo[*f*]quinolinone skeleton to which an *N*,*N*-dialkylaminoalkyl side chain is attached. We were also able to obtain some informations regarding the mechanism of the ET-initiated photocyclization reaction of **1**, through analyses of the product compositions [derived from the starting (*Z*)-**1** and deuteriated (*Z*)-**1a**], as well as of substituent and solvent effects on both the photoreactivities of **1** and the selectivities of the products (**2**–**4**).

EXPERIMENTAL

General methods

^{1}H and ^{13}C NMR and IR spectra were taken with a JEOL JNM-A500 spectrometer and a Hitachi 270-30 infrared spectrophotometer, respectively. Chemical shifts were determined using tetramethylsilane as an internal standard. UV absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer. A cell with a 10-mm pathlength was used. The fluorescence spectra of (*Z*)-**1a** and (*Z*)-**5** at room temperature were measured under nitrogen with a Shimadzu RF-5000 spectrofluorimeter. Elemental analyses were performed on a Perkin-Elmer PE2400 series II CHNS/O analyzer. Methanol and acetonitrile were purified according to the standard procedures and freshly distilled prior to use.[12] All other reagents used were obtained from commercial sources and were of the highest grade available. MM2 calculations were accomplished by using the Mac SPARTAN *Plus* available from Wavefunction, Inc.

General procedure for the synthesis of (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone and (*Z*)-2-(*p*-substituted phenyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolones[9]
N-Acetylglycine or *N*-(*p*-substituted benzoyl)glycine (0.087 mol), 1-naphthaldehyde (16.1 g, 0.103 mol), and sodium acetate (5.3 g, 0.067 mol) were added to acetic anhydride (100 mL) and the resulting mixture was heated at 80–85 °C (*N*-acetylglycine) or 75–80 °C (*N*-aroylglycine) for 6–7 h (*N*-acetylglycine) or 1 h (*N*-aroylglycine) with stirring. The mixture was cooled with ice and the solid separated out was collected by filtration with suction and washed with water, small amounts of cold ethanol and then with dry hexane. After the crude product had been air-dried at room temperature, it was recrystallized from hexane-chloroform to give yellow crystals (30–50%).

(*Z*)-2-Methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. mp 159.0–160.0 ℃. IR (KBr): 1760, 1650, 1260 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (3H, s), 7.54 (1H, dd, *J*= 7.3, 7.9 Hz), 7.58 (1H, dd, *J*= 7.3, 8.6 Hz), 7.61 (1H, dd, *J*= 7.3, 8.6 Hz), 7.88 (1H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 8.6 Hz), 8.02 (1H, s), 8.24 (1H, d, *J*= 8.6 Hz), 8.75 (1H, d, *J*= 7.3 Hz).

(*Z*)-2-(*p*-Anisyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 207.0–208.0 ℃. IR (KBr): 1788, 1644, 1263 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.03 (2H, d, *J*= 8.8 Hz), 7.54–7.66 (3H, m), 7.90 (1H, d, *J*= 7.9 Hz), 7.95 (1H, d, *J*= 7.9 Hz), 8.07 (1H, s), 8.16 (2H, d, *J*= 8.8 Hz), 8.32 (1H, d, *J*= 8.5 Hz), 9.02 (1H, d, *J*= 7.3 Hz).

(*Z*)-2-(*p*-Tolyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 196.0–197.0 ℃. IR (KBr): 1791, 1647, 1170 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.46 (3H, s), 7.34 (2H, d, *J*= 8.6 Hz), 7.56 (1H, dd, *J*= 7.3, 7.9 Hz), 7.62–7.66 (2H, m), 7.90 (1H, d, *J*= 7.9 Hz), 7.96 (1H, d, *J*= 7.9 Hz), 8.10 (2H, d, *J*= 8.6 Hz), 8.11 (1H, s), 8.32 (1H, d, *J*= 8.5 Hz), 9.03 (1H, d, *J*= 7.3 Hz).

(*Z*)-2-Phenyl-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 166.0–167.0 °C. IR (KBr): 1797, 1647, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (2H, dd, *J*= 7.3, 7.6 Hz), 7.55 (1H, dd, *J*= 8.6, 8.6 Hz), 7.62 (1H, dd, *J*= 7.3, 7.3 Hz), 7.63 (1H, dd, *J*= 8.6, 8.6 Hz), 7.64 (1H, dd, *J*= 6.7, 8.6 Hz), 7.90 (1H, d, *J*= 8.6 Hz), 7.97 (1H, d, *J*= 8.6 Hz), 8.13 (1H, s), 8.21 (2H, d, J= 7.6 Hz), 8.31 (1H, d, *J*= 8.6 Hz), 9.03 (1H, d, *J*= 6.7 Hz).

(*Z*)-2-(*p*-Chlorophenyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 215.0–216.0 ℃. IR (KBr): 1794, 1641, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (2H, d, *J*= 8.6 Hz), 7.56 (1H, dd, *J*= 7.3, 7.3 Hz), 7.63–7.66 (2H, m), 7.91 (1H, d, *J*= 7.3 Hz), 7.98 (1H, d, *J*= 7.9 Hz), 8.14 (2H, d, *J*= 8.6 Hz), 8.15 (1H, s), 8.31 (1H, d, *J*= 8.6 Hz), 9.00 (1H, d, *J*= 7.3 Hz).

(*Z*)-2-(*p*-Trifluoromethylphenyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 201.0–202.0 ℃. IR (KBr): 1797, 1641, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (1H, dd, *J*= 6.7, 7.9 Hz), 7.65–7.69 (2H, m), 7.81 (2H, d, *J*= 8.6 Hz), 7.93 (1H, d, *J*= 8.2 Hz), 8.10 (1H, d, *J*= 8.2 Hz), 8.24 (1H, s), 8.33 (2H, d, *J*= 8.6 Hz), 8.33 (1H, d, *J*= 7.9 Hz), 9.02 (1H, d, *J*= 7.6 Hz).

(*Z*)-2-(*p*-Cyanophenyl)-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone. mp 237.0–238.0 ℃. IR (KBr): 2236, 1794, 1641, 1164 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (1H, dd, *J*= 7.3, 7.9 Hz), 7.64–7.68 (2H, m), 7.84 (2H, d, *J*= 8.2 Hz), 7.93 (1H, d, *J*= 7.9 Hz), 8.02 (1H, d, *J*= 7.9 Hz), 8.25 (1H, s), 8.31 (2H, d, *J*= 8.2 Hz), 8.32 (1H, d, *J*= 8.5 Hz), 9.00 (1H, d, *J*= 7.3 Hz).

General procedure for the synthesis of (*Z*)-*N*-acyl-α-dehydro(1-naphthyl)alanine derivatives (1a–j and 5)

(*Z*)-2-Methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1a**–**d** and **5**) or (*Z*)-2-(*p*-substituted phenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1e**–**j**, 0.020 mol) was added to dry chloroform (200 mL) containing *N*,*N*-dialkylaminoalkylamine (for **1a**–**j**) or butylamine (for **5**, 0.021 mol) and the resulting solution was allowed to stand for 1.0 h with stirring in an ice bath. The reaction mixture was concentrated to dryness and the resulting residue was dissolved in ethanol (50 mL) and then treated with activated charcoal powder. After removal of the solvent under reduced pressure, the crystalline solid obtained was recrystallized twice from ethanol-hexane affording colorless crystals (40–70%).

(*Z*)-2-Acetylamino-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1a]. mp 154.0–155.0 ℃. IR (KBr): 3298, 3118, 1620 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 7.0, 7.0 Hz), 1.85 (3H, s), 2.14 (6H, s), 2.27 (2H, t, *J*= 7.0 Hz), 3.22 (2H, dt, *J*= 5.5, 7.0 Hz),

7.52 (1H, s), 7.51–7.59 (4H, m), 7.90 (1H, d, *J*= 7.9 Hz), 7.94–7.97 (2H, m), 8.18 (1H, t, *J*= 5.5 Hz), 9.25 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 26.7, 37.9, 45.1 (2C), 57.1, 123.0, 124.1, 125.4, 125.9, 126.1, 126.2, 128.3, 128.4, 131.0, 131.3, 132.6, 133.1, 164.5, 169.3. Anal. Calcd for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42; N, 12.38. Found: C, 70.36; H, 7.41; N, 12.14.

(*Z*)-2-Acetylamino-*N*-(3'-diethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1b]. mp 143.0–144.0 ℃. IR (KBr): 3304, 3136, 1614 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.96 (6H, t, *J*= 7.0 Hz), 1.61 (2H, tt, *J*= 6.7, 7.0 Hz), 1.84 (3H, s,), 2.43 (2H, t, *J*= 7.0 Hz), 2.46 (4H, q, *J*= 7.0 Hz), 3.21 (2H, dt, *J*= 6.1, 6.7 Hz), 7.48 (1H, s), 7.51–7.58 (4H, m), 7.90 (1H, d, *J*= 8.2 Hz), 7.93–7.96 (2H, m), 8.14 (1H, t, *J*= 6.1 Hz), 9.25 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.6 (2C), 22.9, 26.5, 38.1, 46.3 (2C), 50.2, 123.7, 124.1, 125.4, 125.9, 126.16, 126.23, 128.3, 128.4, 131.0, 131.3, 132.8, 133.1, 164.5, 169.3. Anal. Calcd for $C_{22}H_{29}N_3O_2$: C, 71.90; H, 7.95; N, 11.43. Found: C, 71.67; H, 7.84; N, 11.23.

(*Z*)-2-Acetylamino-*N*-(3'-dipropylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1c]. mp 121.5–123.0 ℃. IR (KBr): 3286, 3148, 1614 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.85 (6H, t, *J*= 7.3 Hz), 1.40 (4H, tq, *J*= 7.3, 7.3 Hz), 1.61 (2H, tt, *J*= 7.0, 7.0 Hz), 1.84 (3H, s,), 2.33 (4H, t, *J*= 7.3 Hz), 2.43 (2H, t, *J*= 7.0 Hz), 3.20 (2H, dt, *J*= 5.5, 7.0 Hz), 7.46 (1H, s), 7.51–7.58 (4H, m), 7.90 (1H, d, *J*= 7.9 Hz), 7.95–7.96 (2H, m), 8.09 (1H, t, *J*= 5.5 Hz), 9.24 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.8 (2C), 19.8 (2C), 22.6, 26.6, 37.9, 51.4, 55.6 (2C), 123.6, 124.1, 125.5, 126.0, 126.2, 126.3, 128.3, 128.4, 131.0, 131.4, 132.8, 133.2, 164.7, 169.4. Anal. Calcd for $C_{24}H_{33}N_3O_2$: C, 72.88; H, 8.41; N, 10.62. Found: C, 72.57; H, 8.35; N, 10.62.

(*Z*)-2-Acetylamino-*N*-(2'-dimethylaminoethyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1d]. mp 150.0–151.0 ℃. IR (KBr): 3298, 3196, 1620 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.83 (3H, s,), 2.17 (6H, s), 2.36 (2H, t, *J*= 7.0 Hz), 3.26 (2H, dt, *J*= 5.5, 7.0 Hz), 7.50–7.57 (5H, m), 7.89 (1H, d, *J*= 7.9 Hz), 7.93–7.95 (3H, m), 9.24 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 37.4, 45.2 (2C), 58.0, 124.16, 124.24, 125.5, 126.0, 126.2, 126.3, 128.38, 128.44, 131.1, 131.3, 132.5, 133.2, 164.7, 169.5. Anal. Calcd for $C_{19}H_{23}N_3O_2$: C, 70.13; H, 7.12; N, 12.91. Found: C, 70.35; H, 7.06; N, 12.85.

(*Z*)-2-(*p*-Anisoylamino)-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1e]. mp 155.0–156.0 ℃. IR (KBr): 3274, 3052, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 6.7, 7.3 Hz), 2.05 (6H, s), 2.26 (2H, t, *J*= 7.3 Hz), 3.25 (2H, dt, *J*= 5.5, 6.7 Hz), 3.79 (3H, s), 6.97 (2H, d, *J*= 8.6 Hz), 7.42 (1H, dd, *J*= 7.3, 7.9 Hz), 7.53–7.58 (2H, m), 7.60 (1H, d, *J*= 7.3 Hz), 7.74 (1H, s), 7.84 (2H, d, *J*= 8.6 Hz), 7.85 (1H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 7.3 Hz), 8.03 (1H, d, *J*= 7.9 Hz), 8.33 (1H, t, *J*= 5.5 Hz), 9.58 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.4, 38.2, 45.0 (2C), 55.3, 57.3, 113.3 (2C), 124.1, 125.3, 125.6, 125.8, 125.9 (2C), 126.3, 128.28, 128.34, 129.6 (2C), 131.1, 131.4, 132.5, 133.1, 161.8, 164.5, 165.5. Anal. Calcd for $C_{26}H_{29}N_3O_3$: C,

72.37; H, 6.77; N, 9.74. Found: C, 72.59; H, 6.38; N, 9.67.

(*Z*)-2-(*p*-Toluoylamino)-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1f]. mp 136.0–137.0 ℃. IR (KBr): 3262, 2944, 1647 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 6.7, 7.3 Hz), 2.05 (6H, s), 2.26 (2H, t, *J*= 7.3 Hz), 2.33 (3H, s), 3.25 (2H, dt, *J*= 5.5, 6.7 Hz), 7.24 (2H, d, *J*= 7.9 Hz), 7.42 (1H, dd, *J*= 7.3, 7.9 Hz), 7.53–7.58 (2H, m), 7.60 (1H, d, *J*= 7.3 Hz), 7.75 (1H, s), 7.76 (2H, d, *J*= 7.9 Hz), 7.85 (1H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 7.3 Hz), 8.02 (1H, d, *J*= 7.9 Hz), 8.34 (1H, t, *J*= 5.5 Hz), 9.66 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 20.9, 26.5, 38.3, 45.1 (2C), 57.4, 124.2, 125.4, 126.0 (3C), 126.4, 127.8 (2C), 128.41, 128.43, 128.7 (2C), 130.9, 131.1, 131.5, 132.5, 133.1, 141.6, 164.6, 166.0. Anal. Calcd for $C_{26}H_{29}N_3O_2$: C, 73.56; H, 7.12; N, 9.90. Found: C, 73.90; H, 6.87; N, 9.66.

(*Z*)-2-Benzoylamino-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1g]. mp 143.0–144.0 ℃. IR (KBr): 3250, 2944, 1644 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 6.7, 6.7 Hz), 2.05 (6H, s), 2.27 (2H, t, *J*= 6.7 Hz), 3.26 (2H, dt, *J*= 5.5, 6.7 Hz), 7.41–7.45 (3H, m), 7.51–7.58 (3H, m), 7.62 (1H, d, *J*= 7.3 Hz), 7.77 (1H, s), 7.84–7.86 (3H, m), 7.93 (1H, d, *J*= 7.3 Hz), 8.03 (1H, d, *J*= 7.9 Hz), 8.34 (1H, t, *J*= 5.5 Hz), 9.74 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.5, 38.2, 45.1 (2C), 57.3, 124.1, 125.3, 125.9 (2C), 126.1, 126.3, 127.7 (2C), 128.0 (2C), 128.4 (2C), 131.0, 131.4, 131.5, 132.3, 133.1, 133.6, 164.4, 166.0. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47. Found: C, 74.84; H, 6.79; N, 10.48.

(*Z*)-2-(*p*-Chlorobenzoylamino)-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1h]. mp 145.0–146.0 ℃. IR (KBr): 3264, 2944, 1650 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 6.7, 6.7 Hz), 2.07 (6H, s), 2.26 (2H, t, *J*= 6.7 Hz), 3.25 (2H, dt, *J*= 6.1, 6.7 Hz), 7.43 (1H, dd, *J*= 7.3, 7.9 Hz), 7.52 (2H, d, *J*= 7.9 Hz), 7.54–7.56 (2H, m), 7.57 (1H, d, *J*= 7.3 Hz), 7.77 (1H, s), 7.86 (1H, d, *J*= 7.9 Hz), 7.86 (2H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 7.3 Hz), 8.02 (1H, d, *J*= 7.3 Hz), 8.34 (1H, t, *J*= 6.1 Hz), 9.81 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.5, 38.0, 45.1 (2C), 57.2, 124.1, 125.3, 125.9 (2C), 126.2, 126.3, 128.1 (2C), 128.35, 128.41, 129.6 (2C), 131.0, 131.3, 132.1, 132.4, 133.1, 136.3, 164.3, 165.0. Anal. Calcd for $C_{25}H_{26}N_3O_2Cl$: C, 68.88; H, 6.01; N, 9.64. Found: C, 68.59; H, 6.02; N, 9.52.

(*Z*)-2-(*p*-Trifluoromethylbenzoylamino)-*N*-(3'-dimethylaminopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1i]. mp 144.0–145.0 ℃. IR (KBr): 3256, 2944, 1650 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.64 (2H, tt, *J*= 6.7, 7.3 Hz), 2.08 (6H, s), 2.26 (2H, t, *J*= 7.3 Hz), 3.25 (2H, dt, *J*= 6.1, 6.7 Hz), 7.44 (1H, dd, *J*= 7.3, 7.9 Hz),, 7.53–7.58 (2H, m), 7.61 (1H, d, *J*= 7.3 Hz), 7.80 (1H, s), 7.83 (2H, d, *J*= 7.3 Hz), 7.87 (1H, d, *J*= 7.9 Hz), 7.94 (1H, d, *J*= 7.3 Hz), 8.03 (2H, d, *J*= 7.3 Hz), 8.03 (1H, d, *J*= 7.3 Hz), 8.36 (1H, t, J= 6.1 Hz), 9.98 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.6, 38.1, 45.1 (2C), 57.1, 123.8 (q, *J*= 273 Hz), 124.1, 124.9, 125.1 (2C, q, *J*= 3 Hz), 125.3, 126.0 (2C), 126.3, 126.6, 128.4, 128.5, 128.6 (2C), 131.0, 131.3 (q, *J*= 33 Hz), 132.0, 133.1, 137.4, 164.2,

164.9. Anal. Calcd for $C_{26}H_{26}N_3O_2F_3$: C, 66.51; H, 5.58; N, 8.95. Found: C, 66.82; H, 5.54; N, 8.60.

(*Z*)-2-(*p*-Cyanobenzoylamino)-*N*-(3'-dimethylamiopropyl)-3-(1-naphthyl)-2-propenamide [(*Z*)-1j]. mp 146.0–147.0 ℃. IR (KBr): 3250, 2944, 2230, 1659 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63 (2H, tt, *J*= 7.3, 7.3 Hz), 2.08 (6H, s), 2.26 (2H, t, *J*= 7.3 Hz), 3.24 (2H, dt, *J*= 5.5, 7.3 Hz), 7.44 (1H, dd, *J*= 7.3, 7.9 Hz), 7.53–7.57 (2H, m), 7.59 (1H, d, *J*= 7.3 Hz), 7.79 (1H, s), 7.87 (1H, d, *J*= 7.9 Hz), 7.94 (1H, d, *J*= 7.3 Hz), 7.94 (2H, d, *J*= 7.9 Hz), 7.96 (2H, d, *J*= 7.9 Hz), 8.01 (1H, d, *J*= 7.3 Hz), 8.37 (1H, t, *J*= 5.5 Hz), 9.99 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.6, 38.0, 45.1 (2C), 57.1, 113.8, 118.1, 124.1, 125.3, 125.9, 126.0, 126.3, 126.6, 128.4, 128.5 (3C), 130.9, 131.2, 131.9, 132.2 (2C), 133.1, 137.6, 164.1, 164.7. Anal. Calcd for $C_{26}H_{26}N_4O_2$: C, 73.22; H, 6.14; N, 13.14. Found: C, 73.61; H, 5.90; N, 12.76.

(*Z*)-2-Acetylamino-*N*-butyl-3-(1-naphthyl)-2-propenamide [(*Z*)-5]. mp 187.0–188.5 ℃. IR (KBr): 3306, 3226, 3156, 1660, 1625 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.90 (3H, t, *J*= 7.3 Hz), 1.33 (2H, tq, *J*= 7.3, 7.6 Hz), 1.48 (2H, tt, *J*= 6.7, 7.6 Hz), 1.83 (3H, s), 3.17 (2H, dt, *J*= 6.4, 6.7 Hz), 7.46 (1H, s), 7.50–7.57 (4H, m), 7.89 (1H, d, *J*= 7.9 Hz), 7.93–7.96 (2H, m), 8.06 (1H, t, *J*= 6.4 Hz), 9.20 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.7, 19.5, 22.6, 31.2, 38.8, 123.7, 124.1, 125.4, 125.9, 126.2 (2C), 128.2, 128.3, 131.0, 131.3, 132.7, 133.1, 164.6, 169.3. Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.54; H, 7.02; N, 9.13.

General procedure for the irradiation of (*Z*)-1a–j and (*Z*)-5

In order to examine the irradiation time dependence of the product distribution and composition, a methanol solution (45 mL) of (*Z*)-**1** (5.0×10^{-3} mol dm^{-3}), placed in a Pyrex vessel, was irradiated under nitrogen at rt with Pyrex-filtered light from a 450 W high-pressure Hg lamp. At suitable time intervals, an aliquot (5 mL) of the solution was pipetted off and concentrated to dryness *in vacuo*. The resulting residue was dissolved in DMSO-d_6 and subjected to ^1H NMR analysis. The composition was estimated from the area ratio of a given ^1H NMR signal for each compound. For the ^2H (D) tracer experiment a MeOD solution (45 mL) of (*Z*)-**1a** (5.0×10^{-3} mol dm^{-3}) was allowed to stand for 12 h and then irradiated for 120 min with Pyrex-filtered light under an atmosphere of prepurified nitrogen. After 120 min irradiation, an aliquot (5 mL) of the solution was pipetted off and concentrated to dryness *in vacuo*. The resulting residue was dissolved in DMSO-d_6 and subjected to ^1H NMR spectral analysis.

On the other hand, a solution (500 mL) of (*Z*)-**1a**–**j** (5.0×10^{-3} mol dm^{-3}) in methanol, placed in a Pyrex vessel, was irradiated for a given period of time under nitrogen with Pyrex-filtered light from a 400 W high-pressure Hg lamp at rt. After 120 min irradiation, an appropriate amount of the solution (5 mL) being irradiated was pipetted off and concentrated to dryness *in vacuo* giving the residue which was subjected to ^1H NMR analysis in DMSO-d_6. The remaining solutions were concentrated to dryness under reduced pressure and the resulting residues were subjected to column chromatography over silica gel (230 mesh, Merck) eluting with ethyl acetate-hexane. For the purpose of isolating the photoproducts, preparative TLC plate (silica gel) was also used. The products isolated were recrystallized from EtOAc or EtOAc-hexane.

Physical and spectroscopic properties of 1,2-dihydrobenzo[*f*]quinolinones (**2a**–**j**), benzo[*f*]isoquinoline (**3a**), 1-azetines (**4e**,**g**–**i**), and (*E*)-isomers [(*E*)-**1a, g**, **j**] are as follows. Any attempts to isolate other products including (*E*)-isomers were not fruitful.

2-Acetylamino-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2a). mp 148.0–149.5 ℃. IR (KBr): 3298, 3052, 1629 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.63–1.75 (2H, m), 1.96 (3H, s), 2.11 (6H, s), 2.18–2.30 (2H, m), 3.00 (1H, dd, *J*= 14.3, 15.5 Hz), 3.66 (1H, dd, *J*= 6.4, 15.5 Hz), 3.99–4.12 (2H, m), 4.58 (1H, ddd, *J*= 6.4, 7.9, 14.3 Hz), 7.45 (1H, dd, *J*= 7.0, 7.6 Hz), 7.54 (1H, d, *J*= 8.9 Hz), 7.55 (1H, dd, *J*= 7.0, 8.5 Hz), 7.91 (1H, d, *J*= 7.6 Hz), 7.92 (1H, d, *J*= 8.9 Hz), 8.00 (1H, d, *J*= 8.5 Hz), 8.35 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 22.6, 25.3, 27.0, 40.8, 45.1 (2C), 48.0, 56.3, 116.1, 118.2, 123.0, 124.6, 127.0, 128.1, 128.3, 129.6, 130.8, 136.2, 168.2, 169.3. Anal. Calcd for $C_{20}H_{25}N_3O_2 \cdot H_2O$: C, 67.20; H, 7.61; N, 11.76. Found: C, 67.06; H, 7.52; N, 11.56.

2-Acetylamino-4-(3'-diethylaminopropyl)-1,2-dihydro-3(4*H*)-benzo[*f*]quinolinone (2b). mp 108.0–109.5 ℃. IR (KBr): 3310, 3064, 1626 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.92 (6H, t, *J*= 7.0 Hz), 1.61–1.71 (2H, m), 1.96 (3H, s), 2.41 (4H, q, *J*= 7.0 Hz), 2.37–2.45 (2H, m), 2.96 (1H, dd, *J*= 14.0, 15.5 Hz), 3.66 (1H, dd, *J*= 6.1, 15.5 Hz), 3.98–4.11 (2H, m), 4.58 (1H, ddd, *J*= 6.1, 7.9, 14.0 Hz), 7.44 (1H, dd, *J*= 7.0, 7.6 Hz), 7.54 (1H, d, *J*= 8.9 Hz), 7.55 (1H, dd, *J*= 7.0, 8.5 Hz), 7.90 (1H, d, *J*= 7.6 Hz), 7.91 (1H, d, *J*= 8.9 Hz), 8.00 (1H, d, *J*= 8.5 Hz), 8.37 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6):δ 11.7 (2C), 22.6, 24.9, 27.0, 40.8, 46.2 (2C), 48.0, 49.5, 116.1, 118.1, 123.0, 124.5, 127.0, 128.0, 128.3, 129.6, 130.8, 136.1, 168.1, 169.3. Anal. Calcd for $C_{22}H_{29}N_3O_2 \cdot 0.5H_2O$: C, 70.18; H, 8.03; N, 11.16. Found: C, 70.15; H, 8.18; N, 11.04.

2-Acetylamino-1,2-dihydro-4-(3'-dipropylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2c). mp 123.5–124.5 ℃. IR (KBr): 3304, 3064, 1629 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.78 (6H, t, *J*= 7.3 Hz), 1.34 (4H, tq, *J*= 7.0, 7.3 Hz), 1.58–1.71 (2H, m), 1.94 (3H, s), 2.26 (4H, t, *J*= 7.0 Hz), 2.38–2.42 (2H, m), 2.94 (1H, dd, *J*= 14.0, 15.5 Hz), 3.63 (1H, dd, *J*= 6.1, 15.5 Hz), 3.98–4.09 (2H, m), 4.56 (1H, ddd, *J*= 6.1, 7.9, 14.0 Hz), 7.43 (1H, dd, *J*= 7.9, 8.5 Hz), 7.51 (1H, d, *J*= 8.5 Hz), 7.52 (1H, dd, *J*= 7.9, 8.5 Hz), 7.89 (1H, d, *J*= 8.5 Hz), 7.89 (1H, d, *J*= 8.5 Hz), 7.98 (1H, d, *J*= 8.5 Hz), 8.33 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6):δ 11.8 (2C), 19.9 (2C), 22.6, 24.9, 27.0, 40.9, 48.0, 50.8, 55.5 (2C), 116.1, 118.2, 123.0, 124.6, 127.0, 128.0, 128.3, 129.6, 130.8, 136.1, 168.1, 169.3. Anal. Calcd for $C_{24}H_{33}N_3O_2$: C, 72.88; H, 8.41; N, 10.62. Found: C, 72.67; H, 8.43; N, 10.53.

2-Acetylamino-1,2-dihydro-4-(2'-dimethylaminoethyl)-3(4*H*)-benzo[*f*]quinolinone (2d). mp 171.0–172.0 ℃. IR (KBr): 3304, 3064, 1629 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.93 (3H, s), 2.18 (6H, s), 2.36–2.48 (2H, m), 2.95 (1H, dd, *J*= 14.3, 15.5 Hz), 3.64 (1H, dd, *J*= 6.1, 15.5 Hz), 4.04–4.10 (1H, m), 4.14–4.20 (1H, m), 4.57 (1H, ddd, *J*= 6.1, 7.9, 14.3 Hz), 7.45 (1H, dd, *J*= 6.8,

7.0 Hz), 7.53 (1H, d, *J*= 9.0 Hz), 7.56 (1H, dd, *J*= 6.8, 8.6 Hz), 7.90 (1H, d, *J*= 7.0 Hz), 7.92 (1H, d, *J*= 9.0 Hz), 7.99 (1H, d, *J*= 8.6 Hz), 8.35 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6):δ 22.6, 26.9, 40.7, 45.4 (2C), 48.0, 56.4, 116.2, 118.3, 123.0, 124.6, 127.0, 128.1, 128.3, 129.6, 130.7, 136.1, 168.3, 169.3. Anal. Calcd for $C_{19}H_{23}N_3O_2$•H_2O: C, 66.45; H, 7.34; N, 12.24. Found: C, 66.55; H, 7.13; N, 12.13.

2-(*p*-Anisoylamino)-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2e). mp 127.0–128.0 ℃. IR (KBr): 3318, 1650 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.66–1.76 (2H, m), 2.12 (6H, s), 2.24–2.33 (2H, m), 3.22 (1H, dd, *J*= 14.7, 15.3 Hz), 3.71 (1H, dd, *J*= 6.1, 15.3 Hz), 3.84 (3H, s), 4.04–4.12 (2H, m), 4.84 (1H, ddd, *J*= 6.1, 7.9, 14.7 Hz), 7.06 (2H, d, *J*= 8.5 Hz), 7.47 (1H, dd, *J*= 6.7, 8.5 Hz), 7.56 (1H, dd, *J*= 6.7, 8.5 Hz), 7.56 (1H, d, J= 9.8 Hz), 7.92 (1H, d, *J*= 8.5 Hz), 7.94 (1H, d, *J*= 9.8 Hz), 7.94 (2H, d, *J*= 8.5 Hz), 8.05 (1H, d, *J*= 8.5 Hz), 8.68 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.3, 26.8, 40.8, 45.0 (2C), 48.3, 55.3, 56.2, 113.5 (2C), 116.1, 118.1, 123.0, 124.5, 126.2, 127.0, 128.1, 128.2, 129.2 (2C), 129.5, 130.7, 136.2, 161.7, 165.6, 168.3. Anal. Calcd for $C_{26}H_{29}N_3O_3$: C, 72.37; H, 6.77; N, 9.74. Found: C, 72.18; H, 6.77; N, 9.43.

2-(*p*-Toluoylamino)-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2f). mp 127.0–128.0 ℃. IR (KBr): 3406, 1653 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.72 (2H, tt, *J*= 7.3, 7.3 Hz), 2.12 (6H, s), 2.28 (2H, t, *J*= 7.3 Hz), 2.39 (3H, s), 3.23 (1H, dd, *J*= 15.3, 15.3 Hz), 3.71 (1H, dd, *J*= 6.1, 15.3 Hz), 4.06 (2H, t, *J*= 7.3 Hz), 4.85 (1H, ddd, *J*= 6.1, 7.9, 15.3 Hz), 7.33 (2H, d, *J*= 8.5 Hz), 7.45 (1H, dd, *J*= 7.3, 7.3 Hz), 7.55 (1H, dd, *J*= 7.3, 8.5 Hz), 7.56 (1H, d, J= 8.5 Hz), 7.87 (2H, d, *J*= 8.5 Hz), 7.92 (1H, d, *J*= 7.3 Hz), 7.94 (1H, d, *J*= 8.5 Hz), 8.05 (1H, d, *J*= 8.5 Hz), 8.75 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 20.9, 25.3, 26.8, 40.8, 45.0 (2C), 48.3, 56.2, 116.1, 118.1, 123.0, 124.5, 127.0, 127.3 (2C), 128.1, 128.2, 128.8 (2C), 129.5, 130.7, 131.2, 136.2, 141.3, 166.0, 168.2. Anal. Calcd for $C_{26}H_{29}N_3O_2$: C, 75.15; H, 7.03; N, 10.11. Found: C, 74.82; H, 7.04; N, 10.11.

2-Benzoylamino-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2g). mp 115.0–116.0 ℃. IR (KBr): 3340, 1656 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.72 (2H, tt, *J*= 7.3, 7.9 Hz), 2.12 (6H, s), 2.23–2.33 (2H, m), 3.24 (1H, dd, *J*= 15.3, 15.3 Hz), 3.73 (1H, dd, *J*= 6.7, 15.3 Hz), 4.02–4.12 (2H, m), 4.86 (1H, ddd, *J*= 6.7, 7.9, 15.3 Hz), 7.46 (1H, dd, *J*= 6.7, 7.9 Hz), 7.53 (2H, dd, *J*= 7.3, 7.3 Hz), 7.56 (1H, dd, J= 6.7, 7.9 Hz), 7.57 (1H, d, *J*= 8.5 Hz), 7.59 (1H, dd, *J*= 7.3, 7.3 Hz), 7.92 (1H, d, *J*= 7.9 Hz), 7.94 (1H, d, *J*= 8.5 Hz), 7.96 (2H, d, *J*= 7.3 Hz), 8.05 (1H, d, *J*= 8.5 Hz), 8.84 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.4, 26.8, 40.9, 45.1 (2C), 48.4, 56.3, 116.1, 118.2, 123.1, 124.6, 127.0, 127.4 (2C), 128.1, 128.25, 128.32 (2C), 129.6, 130.8, 131.4, 134.1, 136.2, 166.2, 168.1. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47. Found: C, 74.84; H, 6.79; N, 10.48.

2-(*p*-Chlorobenzoylamino)-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2h). mp 152.0–153.0 ℃. IR (KBr): 3316, 1629 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.65–1.75 (2H, m), 2.10 (6H, s), 2.22–2.32 (2H, m), 3.21 (1H, dd, *J*= 14.6, 15.3 Hz), 3.71 (1H, dd, *J*= 6.7, 15.3 Hz), 4.03–4.09 (2H, m), 4.83 (1H, ddd, *J*= 6.7, 8.6, 14.6 Hz), 7.44 (1H, dd, *J*= 7.3, 7.9 Hz), 7.55 (1H, dd, *J*= 7.3, 7.9 Hz), 7.55 (1H, d, J= 9.2 Hz), 7.59 (2H, d, *J*= 8.6 Hz), 7.91 (1H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 9.2 Hz), 7.97 (2H, d, *J*= 8.6 Hz), 8.03 (1H, d, *J*= 7.9 Hz), 8.93 (1H, d, *J*= 8.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.4, 26.7, 40.9, 45.1 (2C), 48.6, 56.3, 116.2, 118.2, 123.1, 124.6, 127.1, 128.2, 128.3, 128.5 (2C), 129.3 (2C), 129.6, 130.8, 132.8, 136.2, 136.3, 165.2, 168.0. Anal. Calcd for $C_{25}H_{26}N_3O_2Cl$: C, 68.88; H, 6.01; N, 9.64. Found: C, 68.91; H, 6.03; N, 9.22.

2-(*p*-Trifluoromethylbenzoylamino)-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2i). mp 144.0–145.0 ℃. IR (KBr): 3358, 1659 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.67–1.77 (2H, m), 2.12 (6H, s), 2.33–2.40 (2H, m), 3.24 (1H, dd, *J*= 14.6, 15.3 Hz), 3.75 (1H, dd, *J*= 6.7, 15.3 Hz), 4.05–4.12 (2H, m), 4.87 (1H, ddd, *J*= 6.7, 8.6, 14.6 Hz), 7.46 (1H, dd, *J*= 6.7, 7.3 Hz), 7.56 (1H, dd, *J*= 6.7, 8.5 Hz), 7.57 (1H, d, J= 9.2 Hz), 7.92 (2H, d, *J*= 8.5 Hz), 7.92 (1H, d, *J*= 7.3 Hz), 7.94 (1H, d, *J*= 9.2 Hz), 8.06 (1H, d, *J*= 8.5 Hz), 8.16 (2H, d, *J*= 8.5 Hz), 9.12 (1H, d, *J*= 8.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.4, 26.6, 40.9, 45.1 (2C), 48.6, 56.3, 116.1, 118.1, 123.1, 123.8 (q, *J*= 272 Hz), 124.6, 125.4 (2C, q, *J*= 3 Hz), 127.0, 128.2, 128.3 (2C), 128.6 (q, *J*= 32 Hz), 129.6, 130.7, 131.2, 136.2, 137.9, 165.1, 167.9. Anal. Calcd for $C_{25}H_{26}N_3O_2F_3$: C, 66.51; H, 5.58; N, 8.95. Found: C, 66.50; H, 5.45; N, 8.68.

2-(*p*-Cyanobenzoylamino)-1,2-dihydro-4-(3'-dimethylaminopropyl)-3(4*H*)-benzo[*f*]quinolinone (2j). mp 165.0–166.5 ℃. IR (KBr): 3298, 2230, 1680, 1632 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.72 (2H, tt, *J*= 7.3, 7.3 Hz), 2.12 (6H, s), 2.29 (2H, t, *J*= 7.3 Hz), 3.23 (1H, dd, *J*= 15.3, 15.3 Hz), 3.75 (1H, dd, *J*= 6.1, 15.3 Hz), 4.07 (2H, t, *J*= 7.3 Hz), 4.86 (1H, ddd, *J*= 6.1, 7.9, 15.3 Hz), 7.46 (1H, dd, *J*= 7.3, 7.3 Hz), 7.56 (1H, dd, *J*= 7.3, 7.3 Hz), 7.57 (1H, d, J= 9.2 Hz), 7.93 (1H, d, *J*= 7.3 Hz), 7.94 (1H, d, *J*= 9.2 Hz), 8.03 (2H, d, *J*= 8.6 Hz), 8.05 (1H, d, *J*= 7.3 Hz), 8.11 (2H, d, *J*= 8.6 Hz), 9.15 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.3, 26.5, 40.8, 45.0 (2C), 48.6, 56.2, 113.8, 116.1, 118.0, 118.2, 123.0, 124.5, 127.0, 128.1, 128.18 (2C), 128.21, 129.6, 130.7, 132.4 (2C), 136.1, 138.0, 164.8, 167.8. Anal. Calcd for $C_{26}H_{26}N_4O_2 \cdot H_2O$: C, 70.25; H, 6.35; N, 12.60. Found: C, 70.00; H, 6.03; N, 12.62.

4-Methyl-2-(3'-dimethylaminopropylaminocarbonyl)benzo[*f*]isoquinoline (3a). Oily liquid. IR (neat): 3370, 1704, 1653 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.74 (2H, tt, *J*= 6.7, 7.0 Hz), 2.19 (6H, s), 2.34 (2H, dt, *J*= 6.1, 6.7 Hz), 3.04 (3H, s), 3.44 (2H, t, *J*= 7.0 Hz), 7.82–7.85 (2H, m), 8.11–8.14 (2H, m), 8.18 (1H, d, *J*= 9.1 Hz), 8.92–8.94 (1H, m), 9.13 (1H, s), 9.18 (1H, t, *J*= 6.1 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6):δ 22.6, 26.9, 37.9, 45.2 (2C), 57.4, 112.9, 122.8, 123.8, 126.2, 127.9, 128.7 (2C), 129.0, 129.5, 132.8, 134.6, 144.4, 157.0, 164.0. Anal. Calcd

for $C_{20}H_{23}N_3O•0.5H_2O$: C, 72.70; H, 7.32; N, 12.72. Found: C, 72.60; H, 7.03; N, 12.52.

***cis*-2-(*p*-Anisyl)-4-(3'-dimethylaminopropylaminocarbonyl)-3-(1-naphthyl)-1-azetine (*cis*-4e).** mp 148.0–149.0 ℃. IR (KBr): 3310, 1671 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.67–0.74 (1H, m), 0.75–0.83 (1H, m), 1.72 (2H, dd, *J*= 7.0, 7.0 Hz), 1.88 (6H, s), 2.45–2.59 (2H, m), 3.86 (3H, s), 5.28 (1H, d, *J*= 10.4 Hz), 6.75 (1H, d, *J*= 10.4 Hz), 7.11 (2H, d, *J*= 8.5 Hz), 7.43 (1H, d, *J*= 7.3 Hz), 7.46 (1H, dd, *J*= 7.3, 7.3 Hz), 7.53 (1H, dd, *J*= 7.9, 7.9 Hz), 7.53 (1H, dd, *J*= 7.9, 7.9 Hz), 7.64 (1H, t, *J*= 6.1 Hz), 7.83 (1H, d, *J*= 7.3 Hz), 7.90 (1H, d, *J*= 7.9 Hz), 8.00 (2H, d, *J*= 8.5 Hz), 8.06 (1H, d, *J*= 7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.8, 36.9, 44.9 (2C), 55.4, 56.7, 73.4, 80.1, 114.1 (2C), 119.4, 123.4, 124.0, 124.8, 125.5, 125.9, 128.0, 128.2, 130.1 (2C), 130.2, 132.8, 132.9, 162.1, 164.5, 167.3. Anal. Calcd for $C_{26}H_{29}N_3O_2•H_2O$: C, 72.03; H, 7.21; N, 9.69. Found: C, 72.00; H, 7.09; N, 9.71.

***cis*-2-Phenyl-4-(3'-dimethylaminopropylaminocarbonyl)-3-(1-naphthyl)-1-azetine (*cis*-4g).** mp 138.0–139.0 ℃. IR (KBr): 3262, 1668 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.66–0.73 (1H, m), 0.75–0.82 (1H, m), 1.71 (2H, dd, *J*= 7.3, 7.3 Hz), 1.88 (6H, s), 2.45–2.59 (2H, m), 5.34 (1H, d, *J*= 10.4 Hz), 6.79 (1H, d, *J*= 10.4 Hz), 7.45 (1H, dd, *J*= 6.7, 7.9 Hz), 7.49 (1H, d, *J*= 6.7 Hz), 7.52 (1H, dd, *J*= 6.7, 7.3 Hz), 7.54 (1H, dd, *J*= 6.7, 7.9 Hz), 7.58 (2H, d, *J*= 7.3 Hz), 7.65 (1H, dd, *J*= 7.3, 7.3 Hz), 7.67 (1H, t, *J*= 5.5 Hz), 7.84 (1H, d, *J*= 7.9 Hz), 7.91 (1H, d, *J*= 7.3 Hz), 8.07 (1H, d, *J*= 7.9 Hz), 8.07 (2H, d, *J*= 7.3 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.9, 36.9, 44.8 (2C), 56.6, 73.4, 80.4, 123.5, 124.0, 125.0, 125.6, 126.0, 127.2, 128.1, 128.3 (3C), 128.8 (2C), 130.3, 132.1, 132.80, 132.84, 164.9, 167.3. Anal. Calcd for $C_{25}H_{27}N_3O•H_2O$: C, 74.41; H, 7.24; N, 10.41. Found: C, 74.45; H, 6.99; N, 10.32.

***trans*-2-Phenyl-4-(3'-dimethylaminopropylaminocarbonyl)-3-(1-naphthyl)-1-azetine (*trans*-4g).** A very small amount of the *trans*-isomer isolated did not allow us to measure its melting point and IR spectrum. ^1H NMR (500 MHz, DMSO-d_6): δ 1.60 (2H, tt, *J*= 6.7, 7.0 Hz), 2.10 (6H, s), 2.24 (2H, t, *J*= 6.7 Hz), 3.17 (2H, dt, *J*= 5.5, 7.3 Hz), 4.65 (1H, d, *J*= 6.7 Hz), 6.56 (1H, d, *J*= 6.7 Hz), 7.49 (1H, d, *J*= 6.7 Hz), 7.53 (1H, dd, *J*= 6.7, 7.9 Hz), 7.57 (2H, dd, *J*= 7.3, 7.3 Hz), 7.59–7.60 (2H, m), 7.65 (1H, dd, *J*= 7.3, 7.3 Hz), 7.95 (1H, d, *J*= 7.9 Hz), 8.01–8.05 (2H, m), 8.07 (2H, d, *J*= 7.3 Hz), 8.29 (1H, t, *J*= 5.5 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 26.5, 37.5, 45.0 (2C), 56.8, 76.5, 80.9, 122.5, 122.9, 125.5, 126.2, 126.7 (2C), 128.3 (2C), 128.7, 128.9 (2C), 129.0, 129.3, 132.3, 133.6, 135.4, 163.6, 169.8.

***cis*-2-(*p*-Chlorophenyl)-4-(3'-dimethylaminopropylaminocarbonyl)-3-(1-naphthyl)-1-azetine (*cis*-4h).** mp 137.0–138.0 ℃. IR (KBr): 3280, 1659 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.62–0.69 (1H, m), 0.72–0.80 (1H, m), 1.68 (2H, dd, *J*= 7.3, 7.3 Hz), 1.87 (6H, s), 2.45–2.57 (2H, m), 5.34 (1H, d, *J*= 10.4 Hz), 6.80 (1H, d, *J*= 10.4 Hz), 7.45 (1H, dd, *J*= 7.3, 7.9 Hz), 7.48 (1H, d, *J*= 7.3 Hz), 7.52 (1H, dd, *J*= 6.1, 7.3 Hz), 7.55 (1H, dd, *J*= 6.1, 6.7 Hz), 7.66 (1H, t, *J*= 5.8 Hz),

7.66 (2H, d, *J*= 8.6 Hz), 7.84 (1H, d, *J*= 7.9 Hz), 7.91 (1H, d, *J*= 7.3 Hz), 8.05 (1H, d, *J*= 6.7 Hz), 8.07 (2H, d, *J*= 8.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.8, 36.7, 44.8 (2C), 56.4, 73.3, 80.6, 123.4, 123.8, 124.8, 125.5, 125.9, 126.0, 128.0, 128.2, 128.8 (2C), 130.0 (2C), 130.1, 132.5, 132.7, 136.7, 163.8, 166.9. Anal. Calcd for $C_{25}H_{26}N_3OCl•H_2O$: C, 68.56; H, 6.44; N, 9.59. Found: C, 68.50; H, 6.82; N, 9.44.

***cis*-2-(*p*-Trifluoromethylphenyl)-4-(3'-dimethylaminopropylaminocarbonyl)-3-(1-naphthyl)-1-azetine (*cis*-4i).** mp 138.0–139.0 ℃. IR (KBr): 3310, 1653 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.61–0.69 (1H, m), 0.72–0.80 (1H, m), 1.68 (2H, dd, *J*= 6.7, 6.7 Hz), 1.88 (6H, s), 2.45–2.59 (2H, m), 5.40 (1H, d, *J*= 10.4 Hz), 6.85 (1H, d, *J*= 10.4 Hz), 7.46 (1H, dd, *J*= 7.3, 7.9 Hz), 7.51 (1H, d, *J*= 7.3 Hz), 7.53 (1H, dd, *J*= 7.3, 7.9 Hz), 7.56 (1H, dd, *J*= 7.3, 7.9 Hz), 7.68 (1H, t, *J*= 6.1 Hz), 7.85 (1H, d, *J*= 7.9 Hz), 7.92 (1H, d, *J*= 7.9 Hz), 7.96 (2H, d, *J*= 8.6 Hz), 8.06 (1H, d, *J*= 7.9 Hz), 8.27 (2H, d, *J*= 8.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.8, 36.6, 44.7 (2C), 56.3, 73.4, 80.8, 123.4, 123.80 (q, *J*= 273 Hz), 123.84, 124.8, 125.5, 125.7 (2C, q, *J*= 3 Hz), 125.9, 128.0, 128.2, 129.0 (2C), 130.1, 130.9, 131.7 (q, *J*= 31 Hz), 132.3, 132.7, 163.6, 166.7. Anal. Calcd for $C_{26}H_{26}N_3OF_3•H_2O$: C, 66.23; H, 5.99; N, 8.91. Found: C, 66.43; H, 5.56; N, 8.64.

(*E*)-1a. mp 146.0–147.0 ℃. IR (KBr): 3202, 3028, 1695 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.21 (2H, tt, *J*= 6.7, 7.3 Hz), 1.85 (2H, t, *J*= 7.3 Hz), 1.89 (6H, s), 2.02 (3H, s), 2.92 (2H, dt, *J*= 6.1, 6.7 Hz), 7.37–7.42 (2H, m), 7.47 (1H, s), 7.52 (1H, dd, *J*= 6.7, 7.9 Hz), 7.55 (1H, dd, *J*= 6.7, 7.9 Hz), 7.79 (1H, t, *J*= 6.1 Hz), 7.80 (1H, d, *J*= 7.9 Hz), 7.91 (1H, d, *J*= 7.9 Hz), 8.00 (1H, d, *J*= 7.9 Hz), 9.71 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.5, 25.8, 37.2, 44.9 (2C), 56.6, 112.6, 124.5, 125.3, 125.5, 125.8, 126.0, 127.1, 128.2, 131.2, 132.6, 133.1, 135.0, 164.4, 168.5. Anal. Calcd for $C_{20}H_{25}N_3O_2$: C, 70.77; H, 7.42; N, 12.38. Found: C, 70.34; H, 7.30; N, 12.35.

(*E*)-1g. mp 139.5–140.0 ℃. IR (KBr): 3208, 2950, 1659 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (2H, tt, *J*= 6.7, 7.3 Hz), 1.90 (6H, s), 1.91 (2H, t, *J*= 7.3 Hz), 2.97 (2H, dt, *J*= 6.1, 6.7 Hz), 7.33 (1H, s), 7.45 (1H, dd, *J*= 6.7, 7.3 Hz), 7.47 (1H, d, *J*= 6.7 Hz), 7.54 (2H, dd, *J*= 7.3, 7.3 Hz), 7.55 (1H, dd, *J*= 6.7, 7.3 Hz), 7.57 (1H, dd, *J*= 6.7, 7.9 Hz), 7.61 (1H, dd, *J*= 7.3, 7.3 Hz), 7.83 (1H, t, *J*= 6.1 Hz), 7.83 (1H, d, *J*= 7.3 Hz), 7.93 (1H, d, *J*= 7.9 Hz), 7.98 (2H, d, J= 7.3 Hz), 8.07 (1H, d, *J*= 7.9 Hz), 10.24 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.9, 37.3, 44.8 (2C), 56.7, 115.8, 124.5, 125.3, 125.8 (2C), 126.0, 127.3, 127.7 (2C), 128.2, 128.3 (2C), 131.2, 131.6, 132.1, 133.1, 133.8, 135.1, 164.1, 164.8. Anal. Calcd for $C_{25}H_{27}N_3O_2$: C, 74.79; H, 6.78; N, 10.47. Found: C, 74.40; H, 6.64; N, 10.31.

(*E*)-1j. mp 140.0–141.0 ℃. IR (KBr): 3304, 2944, 2230, 1662 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.60 (2H, tt, *J*= 7.3, 7.3 Hz), 2.55 (6H, s), 2.75 (2H, t, *J*= 7.3 Hz), 3.01 (2H, dt, *J*= 5.5, 7.3 Hz), 7.31 (1H, s), 7.47 (1H, dd, *J*= 7.3, 7.9 Hz), 7.48 (1H, d, *J*= 7.3 Hz), 7.57 (1H, dd, *J*= 7.3, 7.9 Hz), 7.57 (1H, dd, *J*= 7.3, 7.9 Hz), 7.87 (1H, d, *J*= 7.9 Hz), 7.95 (1H, d, *J*= 7.3 Hz), 8.05 (2H, d, *J*=

8.5 Hz), 8.07 (1H, d, *J*= 7.3 Hz), 8.11 (1H, t, *J*= 5.5 Hz), 8.16 (2H, d, *J*= 8.5 Hz), 10.70 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.7, 35.7, 42.3 (2C), 54.6, 114.1, 117.2, 118.2, 124.5, 125.3, 125.8, 125.9, 126.1, 127.6, 128.2, 128.5 (2C), 131.2, 131.7, 132.4 (2C), 133.0, 134.3, 137.5, 163.5, 164.5. Anal. Calcd for $C_{26}H_{26}N_4O_2$•0.5H_2O: C, 71.70; H, 6.25; N, 12.86. Found: C, 72.13; H, 6.10; N, 12.66.

Control Experiments

A methanol solution (100 mL) of (*Z*)-**5** (6.6×10^{-3} mol dm^{-3}), placed in a Pyrex vessel, was irradiated for 40 h under nitrogen at room temperature with Pyrex-filtered light from a 450 W high-pressure Hg lamp. After 40 h irradiation, an aliquot (5 mL) of the solution was pipetted off and concentrated to dryness in vacuo. The resulting residue was dissolved in DMSO-d_6 and subjected to ^{1}H NMR analysis. The remaining solution was concentrated to dryness under reduced pressure and the resulting residue was subjected to preparative thin-layer chromatography over silica gel (ethyl acetate-hexane). This procedure allowed us to isolate (*Z*)-**5**, (*E*)-**5**, **7** (major product), and **8**. These products were recrystallized from EtOAc-hexane. Physical and spectroscopic properties of **7**, **8** and (*E*)-isomer are shown below.

2-Acetylamino-4-butyl-3(4*H*)-benzo[*f*]quinolinone (7). mp 163.0–164.0 ℃. IR (KBr): 3346, 1620, 1600 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (3H, t, *J*= 7.3 Hz), 1.53 (2H, tq, *J*= 7.3, 7.6 Hz), 1.82 (2H, tt, *J*= 7.6, 7.9 Hz), 2.29 (3H, s), 4.50 (2H, t, *J*= 7.9 Hz), 7.54 (1H, dd, *J*= 6.7, 8.2 Hz), 7.54 (1H, d, *J*= 9.2 Hz), 7.66 (1H, dd, *J*= 6.7, 8.6 Hz), 7.87 (1H, d, *J*= 8.2 Hz), 7.91 (1H, d, *J*= 9.2 Hz), 8.47 (1H, d, *J*= 8.6 Hz), 8.65 (1H, s), 9.68 (1H, s). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.8, 20.3, 25.0, 30.2, 43.7, 114.2, 115.8, 116.1, 122.6, 125.6, 127.7, 127.8, 128.4, 129.5, 129.8, 130.0, 133.1, 157.3, 169.4. Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.55; H, 6.37; N, 8.90.

4-Methyl-2-(butylaminocarbonyl)benzo[*f*]isoquinoline (8). mp 61.5–62.5 ℃. IR (KBr): 3382, 1668 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.94 (3H, t, *J*= 7.3 Hz), 1.37 (2H, tq, *J*= 7.3, 7.6 Hz), 1.60 (2H, tt, *J*= 7.0, 7.6 Hz), 3.04 (3H, s), 3.41 (2H, dt, *J*= 6.1, 7.0 Hz), 7.81–7.85 (2H, m), 8.12 (1H, d, *J*= 9.2 Hz), 8.11–8.15 (1H, m), 8.17 (1H, d, *J*= 9.2 Hz), 8.83 (1H, t, *J*= 6.1 Hz), 8.90–8.93 (1H, m), 9.12 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.7, 19.6, 22.6, 31.5, 38.6, 113.0, 122.8, 123.8, 126.2, 127.9, 128.65, 128.71, 129.1, 129.5, 132.9, 134.6, 144.4, 157.0, 164.1. Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58. Found: C, 77.85; H, 7.09; N, 9.74.

(*E*)-5. mp 148.0–149.0 ℃. IR (KBr): 3250, 1650, 1629 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.66 (3H, t, *J*= 7.3 Hz), 0.88 (2H, tq, *J*= 7.3, 7.6 Hz), 1.06 (2H, tt, *J*= 7.0, 7.3 Hz), 2.00 (3H, s), 2.87 (2H, dt, *J*= 6.1, 7.0 Hz), 7.36–7.40 (2H, m), 7.43 (1H, s), 7.49–7.57 (2H, m), 7.75 (1H, t, *J*= 6.1 Hz), 7.77–7.79 (1H, m), 7.89 (1H, d, *J*= 7.3 Hz), 7.98 (1H, d, *J*= 7.6 Hz), 9.69 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.6, 19.4, 23.5, 30.3, 38.3, 112.6, 124.6, 125.3, 125.6, 125.8, 126.0, 127.1, 128.2, 131.3, 132.6, 133.1, 135.1, 164.4, 168.6. Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.29; H, 7.19; N, 9.14.

ACKNOWLEDGMENT

This research was partially supported by a "High-Tech Research Project" from the Ministry of Education, Sports, Culture, Science and Technology, Japan.

REFERENCES

1. P. S. Mariano and J. L. Stavinoha, 'Synthetic Organic Photochemistry,' ed. by W. M. Horspool, Plenum Press, New York, 1984, pp. 145–257.
2. F. D. Lewis, *Acc. Chem. Res.*, 1979, **12**, 152; F. D. Lewis and G. D. Reddy, *J. Am. Chem. Soc.*, 1989, **111**, 6465; F. D. Lewis, G. D. Reddy, and D. M. Bassani, *J. Am. Chem. Soc.*, 1993, **115**, 6468; F. D. Lewis, D. M. Bassani, and G. D. Reddy, *J. Org. Chem.*, 1993, **58**, 6390; F. D. Lewis, D. Reddy, D. M. Bassani, S. Schneider, and M. Gahr, *J. Am. Chem. Soc.*, 1994, **116**, 597; F. D. Lewis, D. M. Bassani, E. L. Burch, B. E. Cohen, J. A. Engleman, G. D. Reddy, S. Schneider, W. Jaeger, P. Gedeck, and M. Gahr, *J. Am. Chem. Soc.*, 1995, **117**, 660.
3. C. Shin, Y. Yonezawa, and M. Ikeda, *Bull. Chem. Soc. Jpn.* 1986, **59**, 3573; C. Shin, N. Takahashi, and Y. Yonezawa, *Chem. Pharm. Bull.*, 1990, **38**, 2020; U. Schmidt, H. Griesser, V. Leitenberger, A. Lieberknecht, R. Mangold, R. Meyer, and B. Riedl, *Synthesis*, **1992**, 487; F. Effenberger, J. Kuehlwein, M. Hopf, and U. Stelzer, *Liebigs Ann. Chem.*, **1993**, 1303.
4. C. Shin, Y. Nakajima, T. Haga, and Y. Sato, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3917; Y. Sato, Y. Nakajima, and C. Shin, *Heterocycles*, 1992, **33**, 589.
5. a) K. Kubo, S. Yaegashi, K. Sasaki, T. Sakurai, and H. Inoue, *Tetrahedron Lett.*, 1996, **37**, 5917; b) K. Kubo M. Koshiba, H. Hoshina, and T. Sakurai, *Heterocycles*, 1998, **48**, 25; c) H. Hoshina, K. Kubo, A. Morita, and T. Sakurai, *Tetrahedron*, 2000, **56**, 2941; d) H. Hoshina, H. Tsuru, K. Kubo, T. Igarashi, and T. Sakurai, *Heterocycles*, 2000, **53**, 2261.
6. T. Sakurai, Y. Morioka, K. Maekawa, and K. Kubo, *Heterocycles*, 2000, **53**, 271; K. Maekawa, T. Igarashi, K. Kubo, and T. Sakurai, *Tetrahedron*, 2001, **57**, 5515.
7. K. Noda, Y. Shimohigashi, and N. Izumiya, 'The Peptides-Analysis, Synthesis, Biology,' Vol. 5, ed. by E. Gross and J. Meienhofer, Academic Press, New York, 1983, pp. 285–339.
8. T. Sakurai, K. Miyoshi, M. Obitsu, and H. Inoue, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 46; K. Miyoshi, K. Kubo, T. Sakurai, and H. Inoue, *Nippon Kagaku Kaishi*, **1999**, 37 and references cited therein; K. Ozawa, K. Miyoshi, K. Kubo, T. Igarashi, and T. Sakurai, *Nippon Kagaku Kaishi*, **2000**, 511.
9. Y. S. Rao and R. Filler, *Synthesis*, **1975**, 749; B. Rzeszotarska, J. Karolak-Wojciechowska, M. A. Broda, Z. Galdecki, B. Trzezwinska, and A. E. Koziol, *Int. J. Peptide Protein Res.*, 1994, **44**, 313.
10. A. Kolbe, P. Kaps, and M. Plass, *Z. Phys. Chem.*, 1995, **191**, 191.
11. W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, pp. 323–350; T. Sakurai, K. Wada, and H. Inoue, *Nippon Kagaku Kaishi*, **1993**, 728.
12. J. A. Riddick, W. B. Bunger, and T. K. Sakano, 'Organic Solvents,' 4th ed. Wiley, Chichester, 1986.
13. G. R. Lenz, *Synthesis*, **1978**, 489; S. Naruto and O. Yonemitsu, *Chem. Pharm. Bull.*, 1980, **28**,

900; T. Hamada, Y. Okuno, M. Ohmori, T. Nishi, and O. Yonemitsu, *Chem. Pharm. Bull.*, 1981, **29**, 128; I. Ninomiya, C. Hashimoto, T. Kiguchi, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 941; K. Jones, M. Thompson, and C. Wright, *J. Chem. Soc., Chem. Commun.*, **1986**, 115; M. Mascal and C. J. Moody, *J. Chem. Soc., Chem. Commun.*, **1988**, 587; G. P. Johnson and B. A. Marples, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 3399; A. L. Beck, M. Mascal, C. J. Moody, A. M. Z. Slawin, D. J. Williams, and W. J. Coates, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 797; A. L. Beck, M. Mascal, C. J. Moody, and W. J. Coates, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 813; R. Rezaie, J. B. Bremner, G. K. Blanch, B. W. Skelton, and A. H. White, *Heterocycles*, 1995, **41**, 959; M.-L. Bennasar, E. Zulaica, A. Ramírez, and J. Bosch, *Heterocycles*, 1996, **43**, 1959; B. E. Ali, K. Okuro, G. Vasapollo, and H. Alper, *J. Am. Chem. Soc.*, 1996, **118**, 4264; T. Nishio, H. Asai, and T. Miyazaki, *Helv. Chim. Acta*, 2000, **83**, 1475; H. Zhao, A. Thurkauf, J. Braun, R. Brodbeck, and A. Kieltyka, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 2119; C. Jia, D. Piao, T. Kitamura, and Y. Fujiwara, *J. Org. Chem.*, 2000, **65**, 7516.

14. I. Ninomiya and T. Naito, *Heterocycles*, 1981, **15**, 1433; T. Naito, Y. Tada, and I. Ninomiya, *Heterocycles*, 1984, **22**, 237.