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Electron transfer-initiated photocyclization of substituted *N*-acetyl-α-dehydro(1-naphthyl)alanines to 1,2-dihydrobenzo[*f*]quinolinone derivatives: scope and limitations

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Abstract—The irradiation of substituted *N*-acetyl-α-dehydro(1-naphthyl)alanines (**1**) in MeOH containing triethylamine with Pyrex-filtered light gave 1,2-dihydrobenzo[*f*]quinolinones (**2**) in preference to benzo[*f*]isoquinolines (**3**) and 1-azetines (**4**). Analysis of substituent effects on the product compositions revealed that the selectivity of **2** has a strong tendency to decrease with increasing steric bulkiness of the alkyl substituent introduced into the starting (*Z*)-**1**. From control and fluorescence quenching experiments it was shown that the photocyclization reaction of **1** affording **2** proceeds by an electron-transfer mechanism. The mechanism of this novel cyclization was discussed mainly based on substituent and solvent effects on both the reactivities of the excited singlet-state **1** and the selectivities of the products **2**–**4**. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Synthetic organic photochemistry has continued to contribute to the development of efficient and selective transformations for the preparation of natural products as well as complicated molecules which could not have been synthesized by conventional methods.[1] It is well-known that many of naturally occurring α,β-unsaturated-α-amino acids (α-dehydroamino acids) and α-dehydropeptides possess a variety of biological activities,[2] allowing us to expect the potential pharmacological and physiological usefulness of these dehydroamino acid-derived products. Efficient synthetic routes to α-dehydroamino acids and their derivatives have been discovered,[3] whereas there has been only limited preliminary investigation of the photochemistry of these dehydroamino acid derivatives.[4] In this sense, the photochemistry of substituted α-dehydroamino acids is an unexplored field of research. Accordingly, systematic study is required to characterize the photochemical processes of substituted α-dehydroamino acids.

In recent years, much attention has been devoted to the synthetic application of excited-state processes initiated by electron transfer (ET), owing to the fact that many photo-induced ET reactions proceed in high chemical and quantum yields enabling the construction of heteroatom-containing polycyclic compounds.[5,6] In the course of our systematic study towards the characterization of the excited-state reactions of substituted α-dehydrophenylalanines, we have discovered interesting photocyclization reactions giving isoquinoline and/or 1-azetine derivatives.[7] If we introduce a naphthyl group (instead of a phenyl) into α-dehydroamino acids, it is expected that we might be able to explore ET-initiated photoreactions of naphthyl-substituted α-dehydroamino acid derivatives in the presence of an aliphatic amine.[8] Taking into account the fact that aromatic olefins such as styrene and stilbene derivatives show diverse excited-state reactivities of synthetic utility,[5,9] our attention is focused on the photo-induced ET reactions of *N*-acetyl-α-dehydro(1-naphthyl)alanine derivatives (**1**) in the presence of triethylamine (TEA) which may serve as an electron donor. In this paper, we highlight the scope and limitations of ET photochemistry of **1** in the synthesis of heterocyclic compounds having the benzoquinolinone skeleton, as well as the mechanism of the novel photocyclization reactions initiated by ET.

2. Results and discussion

2.1. Product distribution and composition in methanol

The starting (*Z*)-isomers **1a**–**k** were prepared in good yields

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Keywords: amino acids and derivatives; photochemistry; electron transfer; dihydrobenzoquinolinones; benzoisoquinolines.

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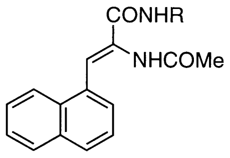
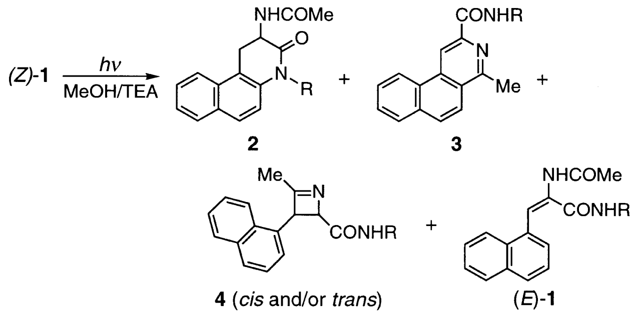


(*Z*)-**1a–k**

1a (R= H); **1b** (R= Me); **1c** (R= Et); **1d** (R= Pr);
1e (R= *i*-Pr); **1f** (R= Bu); **1g** (R= $PhCH_2$);
1h (R= 4-$OMeC_6H_4CH_2$); **1i** (R= 4-$CF_3C_6H_4CH_2$)
1j (R= *t*-Bu); **1k** (R= Ph)

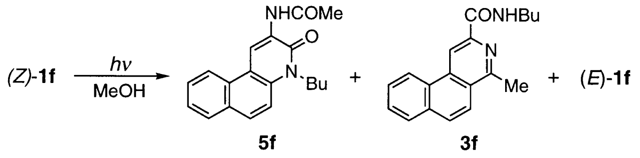
by the ring-opening reactions of (*Z*)-1-naphthyl-substituted oxazolones with primary amines.[10] After a nitrogen-purged MeOH solution of **1f** (5.0×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}) was irradiated with Pyrex-filtered light (>280 nm) from a 400 W high-pressure Hg lamp for 1.5 h at room temperature, the product mixture obtained was subjected to column chromatography over silica gel, which allowed us to isolate the starting (*Z*)-**1f** (6%, isolated yield), (*E*)-isomer of **1f** (5%), substituted 1,2-dihydrobenzo[*f*]quinolinone **2f** (45%) and benzo[*f*]isoquinoline **3f** (14%). The structures of the isolated products were determined based on their spectroscopic and physical properties and were confirmed by the ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectra of these products. A careful ^{1}H NMR analysis of the product mixture suggested the detectable formation of the *cis*-1-azetine isomer **4f** whose ring-proton signals with the $J_{3,4}$ value of 10.7 Hz were detected at 5.04 and 6.50 ppm,[7c] though attempts to isolate **4f** from the mixture were unsuccessful owing to its poor yield (Scheme 1). The same product distribution was obtained by the irradiation of other dehydronaphthylalanine derivatives **1a–e** and **1g–i**, but **1j**,**k** gave negligible amounts of dihydrobenzoquinolinone derivatives.



Scheme 1.

Table 1. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**If** in MeOH–TEA at room temperature

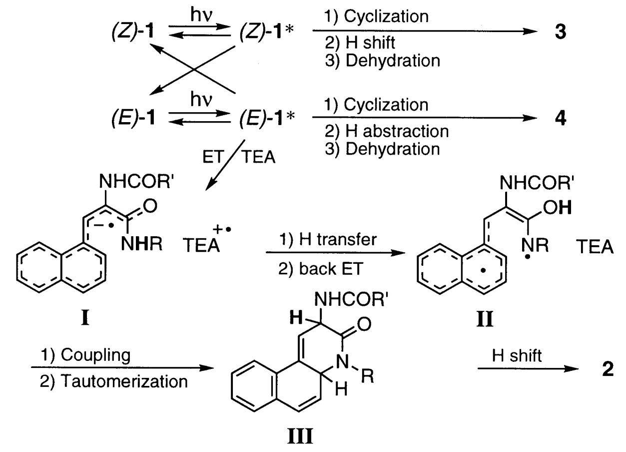
Compound	Irradiation time (h)							
	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
(*Z*)-**1f**	100	60.7	43.5	34.2	27.3	18.0	9.3	4.0
(*E*)-**1f**	0	31.6	38.0	35.8	32.0	22.5	11.8	5.6
2f	0	4.3	11.7	20.4	28.8	43.8	59.3	69.0
3f	0	3.2	6.5	9.0	11.0	14.5	17.8	19.6
cis-**4f**	0	0.1	0.3	0.6	0.9	1.2	1.8	1.8



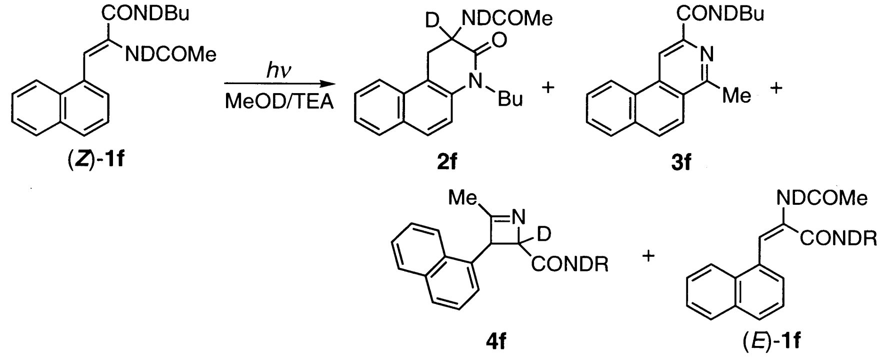
Scheme 2.

The finding that the photoproducts **2–4** are stable enough such that they undergo only negligible decomposition under the irradiation conditions employed (450 W high-pressure Hg lamp; Pyrex glass filter; [(*Z*)-**1**]=3.75×10^{-3} mol dm^{-3}; [TEA]=0.10 mol dm^{-3}) made it possible to monitor the reactions by means of ^{1}H NMR spectroscopy, as typically shown in Table 1. The result obtained for (*Z*)-**1f** demonstrates the rapid production of (*E*)-**1f** and the subsequent increase in compositions for **2f–4f** with the decrease of (*E*)- and (*Z*)-isomer compositions, being consistent with the mechanism in which these excited-state isomers serve as precursors of these products. On the other hand, there was no formation of the dihydrobenzoquinolinone derivative **2f** when a nitrogen-purged MeOH solution of (*Z*)-**1f** (6.6×10^{-3} mol dm^{-3}) containing no TEA was irradiated with Pyrex-filtered light from a 450 W high-pressure Hg lamp for 40 h (^{1}H NMR analysis), suggesting that ET from TEA to the excited-state naphthylmethylene moiety in **1f** participates in the appearance of **2f** as the primary process. Instead, the benzo[*f*]quinolinone derivative **5f** was isolated as major product (22%) along with **3f** (15%), (*E*)-**1f** (14%) and (*Z*)-**1f** (10%) (Scheme 2). A ^{1}H NMR analysis of the product mixture revealed that the presence of unknown products makes it very difficult to detect proton signals attributable to **4f**. The structure of **5f** 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. It is likely 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 **5f**. However, 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.

On the other hand, the fluorescence of (*Z*)-**1f** (5.0×10^{-5} mol dm^{-3}) in nitrogen-saturated MeOH was quenched by TEA (0.020–0.10 mol dm^{-3}; excitation wavelength, 280 nm) according to the Stern–Volmer equation, $I_0/I=1+4.5\pm0.5$[TEA], where I and I_0 refer to the fluorescence intensities of **1f** with and without TEA. It is evident from a comparison of the UV absorption spectrum of TEA with that of (*Z*)-**1f** that the first singlet excitation energy of the latter molecule is much lower than that of the former and, hence, the fluorescence quenching observed is due to ET but not due to singlet–singlet energy transfer. Unfortunately, we could not determine the fluorescence lifetimes of substituted naphthylalanines owing to their weak or very weak emissions. Furthermore, it is well-known that the photoinduced ET reactions of amine–aromatic systems are thermodynamically favorable process and proceed



Scheme 3.



Scheme 4.

efficiently to give mechanistically interesting products.[1,6,8] Accordingly, these considerations (in addition to the previous results[7] and the fact that no **2f** is formed without TEA) lead us to propose Scheme 3 in which ET from the ground-state TEA to 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 transfer from the amide nitrogen to the amide carbonyl oxygen within the intermediate **I** and the subsequent back ET to TEA radical cation affords TEA and 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*-alkyl amide hydrogen in the starting **1** should migrate to the 2-position of the benzoquinolinone ring upon forming **2**, and that the TEA concentration should remain constant during the reaction. After the H–D exchange reaction for the amide protons of (*Z*)-**1f** (3.75×10^{-3} mol dm^{-3}) in MeOD–TEA (0.10 mol dm^{-3}) was completed (12 h incubation), deuteriated **1f** was irradiated with Pyrex-filtered light from a 450 W high-pressure Hg lamp for 5.0 h at room temperature. ^{1}H NMR spectra of the product mixture in DMSO-d_6, obtained after usual work-up, clearly showed disappearance of the 4.56 ppm signal which was ascribed to the proton attached to the 2-position of the ring (Scheme 4). The same results were obtained by the irradiation of a MeOD solution of (*Z*)-**1a** having no alkyl substituent attached to the amide nitrogen, as well as by the irradiation of deuteriated **1f** in MeCN. Furthermore, a ^{1}H NMR analysis of the reaction mixture obtained by the irradiation of a CD_3OD solution of (*Z*)-**1f** (2.5×10^{-2} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}) and 1,4-dioxane (internal standard, 0.10 mol dm^{-3}) for a given period of time showed no sign of a change in this amine concentration during the reaction. These findings are consistent with our prediction, thereby substantiating the mechanism proposed for the formation of **2**.

If the rate for the cyclization reaction from the excited-state (*E*)-isomer via ET does not differ greatly from that for the isomerization into the (*Z*)-isomer, Scheme 3 may allow us to expect that the use of (*E*)-**1f** as the starting isomer enhances the composition of **2f** relative to that of **3f** at the early stage of the reaction. A nitrogen-purged MeOH solution of (*E*)-**1f** (3.75×10^{-3} mol dm^{-3}) was irradiated under the same conditions as those for the irradiation of (*Z*)-**1f** and the results obtained are shown in Table 2. A comparison of the composition of each compound given in Tables 1 and 2 (0.5 h irradiation) reveals that the reaction starting from the excited-state (*E*)-isomer increases significantly the relative composition of **2f** [**2f**/**3f**=1.3 for (*Z*)-**1f** and 17.6 for (*E*)-**1f**] and then the composition of **4f** is also increased by a factor of about 5. In addition, prolonged irradiation reduces the difference in product composition between the (*Z*)- and (*E*)-isomers. These findings are in accord with our expectation and, hence, lead us to conclude that the isomerization is not so fast as compared to the ET and cyclization processes in which the excited-state (*E*)-isomer serves as a precursor of dihydrobenzoquinolinone and 1-azetine derivatives. It is

Table 2. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*E*)-**If** in MeOH–TEA at room temperature

Compound	Irradiation time (h)							
	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
(*Z*)-**1f**	0	26.9	30.6	27.4	21.7	12.7	6.1	1.8
(*E*)-**1f**	100	56.0	40.2	31.4	25.5	15.6	8.1	2.6
2f	0	15.8	25.8	35.4	44.6	60.2	71.7	80.1
3f	0	0.9	2.5	4.8	6.8	9.9	12.3	13.8
cis-**4f**	0	0.5	0.8	1.0	1.4	1.6	1.8	1.7

Table 3. Substituent effects on the composition of each compound obtained by the irradiation of the strating (*Z*)-**1** in MeOH containing TEA at room temperature

Compound	Irradiation time (h)	Composition (%)					
		(*Z*)-**1**	(*E*)-**1**	**2**	**3**	*cis*-**4**	*trans*-**4**
1a (R=H)	0.5	59.1	35.7	3.9	0.7	0.6	0.0
	5.0	2.2	3.4	76.3	13.0	5.2	0.0
1b (R=Me)	0.5	71.3	22.9	4.0	1.8	0.0	0.0
	5.0	1.4	1.7	85.0	11.0	0.9	0.0
1c (R=Et)	0.5	69.8	25.1	3.0	2.1	0.0	0.0
	5.0	4.1	4.9	74.5	14.9	1.5	0.0
1d (R=Pr)	0.5	67.9	27.0	2.8	2.2	0.0	0.0
	5.0	5.7	7.3	68.4	17.4	1.2	0.0
1e (R=*i*-Pr)	0.5	65.5	31.3	0.0	3.2	0.0	0.0
	5.0	8.9	14.2	43.3	26.2	5.8	1.5
1f (R=Bu)	0.5	60.7	31.6	4.3	3.2	0.1	0.0
	5.0	4.0	5.6	69.0	19.6	1.8	0.0
1g (R=$PhCH_2$)	0.5	61.9	32.4	3.2	2.5	0.0	0.0
	5.0	1.8	3.5	70.8	20.8	3.1	0.0
1h (R=4-$OMeC_6H_4CH_2$)	0.5	56.8	34.7	5.7	2.9	0.0	0.0
	5.0	3.7	4.4	69.2	21.6	1.2	0.0
1i (R=4-$CF_3C_6H_4CH_2$)	0.5	59.9	35.5	2.5	2.1	0.0	0.0
	5.0	7.2	9.8	62.7	16.5	3.7	0.0
1j (R=*t*-Bu)	1.0	52.1	40.0	0.0	6.4	0.7	0.7
	9.0	14.8	20.8	0.0	47.8	10.3	6.2
1k (R=Ph)	1.0	82.2	17.1	0.0	0.7	0.0	0.0
	9.0	44.1	34.5	0.0	10.4	9.6	1.3

very likely that the (*Z*)-isomer radical anion generated by ET from TEA reverts to the starting (*Z*)-**1f** through back ET to the TEA radical cation, owing to the unfavorable configuration of this radical anion for the cyclization reaction eventually affording **2f**.

2.2. Substituent effects on the product composition

In order to shed light on the scope and limitations of ET-induced cyclization reactions in the synthesis of substituted 1,2-dihydrobenzo[*f*]quinolinones, we investigated substituent effects on the product composition obtained in MeOH (Table 3). Table 3 clearly shows that both the photoreactivities of the (*Z*)- and (*E*)-isomers have a tendency to decrease with increasing steric bulkiness of the alkyl substituent attached to the amide nitrogen (R=Me→*i*-Pr→*t*-Bu), whereas this increase in steric bulkiness accelerates the isomerization into the (*E*)-isomer. These findings suggest that the introduction of sterically bulky substituent at the olefinic carbon of (*Z*)-**1** enhances the rate for deactivation of the excited-state (*Z*)-isomer accompanying its isomerization. It should be also pointed out here that the phenyl substituent in **1k** substantially lowers the excited-state reactivity of this naphthylalanine derivative, and that the reactivity of **1g** (R=$PhCH_2$) undergoes electronic effects of the methoxy (**1h**) and trifluoromethyl (**1i**) groups to only a very small extent.

Because both the 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 was estimated by employing the compositions obtained at three different irradiation times (3.0, 4.0 and 5.0 h for **1a**–**i**; 5.0, 7.0 and 9.0 h for **1j**,**k**) and its average value is collected in Table 4. Interestingly, the selectivity of **2**, except **2a**, decreases with an increse in steric bulkiness of the substituent R: **2b**>**2c**>**2d** **2f**≈**2g**≈**2h**≈**2i** **2e**≫**2j**=**2k**. This decrease in selectivity is reflected in the enhanced selectivity for substituted benzoisoquinolines (**3**) and 1-azetines (**4**), being consistent with the mechanism in which ET to the excited-state (*E*)-**1** occurs in competition with both the cyclization giving eventually **4** and the isomerization into (*Z*)-**1**, as shown in Scheme 3. In addition, the introduction of bulky *tert*-butyl (**1j**) and phenyl (**1k**) groups into **1** completely inhibits the appearance of the corresponding benzoquinolinone derivative **2** (the selectivity of **2** becomes zero). Because the fluorescence of **1j** (5.0×10^{-5} mol dm^{-3}) is also quenched by TEA ($I_0/I=1+3.0\pm0.4$[TEA]; [TEA]=0.020–0.10 mol dm^{-3}; excitation wavelength, 273 nm), ET from TEA to the excited-state (*E*)-**1j** should take place giving the **1j** radical anion and TEA radical cation pair **I** (Scheme 3). Taking into account that the enol-type biradical **II** may adopt an approximately planar structure, it is reasonable to conclude that the bulky *tert*-butyl and phenyl substituents exert their

Table 4. Substituent effects on the selectivity of each product obtained by the irradiation of the starting (*Z*)-**1**

Compound	Selectivity (%)			
	2	**3**	*cis*-**4**	*trans*-**4**
1a	80.5	12.7	6.7	0.0
1b	87.7	11.4	0.9	0.0
1c	81.6	16.7	1.7	0.0
1d	77.3	21.2	1.6	0.0
1e	54.4	36.0	7.6	2.1
1f	75.0	23.0	2.1	0.0
1g	74.5	22.2	3.3	0.0
1h	74.5	23.4	2.1	0.0
1i	75.0	20.6	4.3	0.0
1j	0.0	74.5	15.8	9.7
1k	0.0	48.3	45.1	6.6

Table 5. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**1f** in MeCN–TEA at room temperature

Compound	Irradiation time (h)							
	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0
(*Z*)-**1f**	100	77.4	70.0	65.0	60.6	53.1	44.6	38.0
(*E*)-**1f**	0	20.1	24.3	26.2	27.5	27.8	28.1	26.3
2f	0	1.6	3.6	5.8	8.1	12.7	19.3	25.3
3f	0	0.9	2.0	3.1	3.9	6.3	8.0	10.5
cis-**4f**	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

great steric effects on the coupling process of **II** so as to completely inhibit this process. This conclusion is substantiated by MM2 calculations of **2f** and **2j** (which demonstrate that the replacement of butyl group by *tert*-butyl as the substituent R results in a great destabilization of the former dihydrobenzoquinolinone derivative (57.6 kJ mol^{-1})) and, thus, provides a piece of evidence for the mechanism shown in Scheme 3. There were negligible products other than (*E*)-**1**, **3** and **4** in the reaction mixtures obtained by the irradition of **1j** and **1k** in the presence of TEA (^{1}H NMR analysis). This observation suggests that on prevention of the cyclization of **II** affording **2** via **III**, the intermediate **II** eventually reverts to the (*E*)-isomer. On the other hand, contrary to our expectation the starting **1a** having no *N*-alkyl substituent afforded **2a** in lower selectivity than that of **2b** (Table 4). The finding that the selectivity of **4a** is much larger than that of **4b** confirms that the substitution of hydrogen for the methyl group lowers the relative rate of ET from TEA to the excited-state (*E*)-isomer, probably owing to the decreased reactivity of the intermediate **I** toward intramolecular hydrogen transfer (Scheme 3).

2.3. Solvent effects on the product composition

It was previously shown that ET from the tertiary amino nitrogen takes place more efficiently in MeCN than in MeOH because of the formation of hydrogen bonding in the latter solvent.[8,11] Thus, we may expect the enhancement of both the photoreactivity of (*Z*)-**1** and the selectivity of the dihydrobenzoquinolinone derivative **2**. In Table 5 are shown compositions of **1f**–**4f** obtained by the irradiation of (*Z*)-**1f** (3.75×10^{-3} mol dm^{-3}) in MeCN containing TEA (0.10 mol dm^{-3}) under the same conditions. A comparison of Tables 1 and 5 reveals that the excited-state reactivities of both isomers are much higher in the protic polar solvent, MeOH, than in the aprotic polar solvent, MeCN, being not consistent with our expectation. Additionally, the latter solvent lowers not only the relative rate for the *Z*→*E* isomerization (0.5 h irradiation) but also the selectivity of **2f** (75.0→69.4%, average values). Similar results were obtained with (*Z*)-**1a** (R=H) and (*Z*)-**1g** (R=PhCH$_2$). These observations cannot be explained in terms of the disappearance of hydrogen-bonding solvation of TEA in MeCN. Since the amide carbonyl oxygen has been found to readily forms a hydrogen bond to a protic solvent molecule,[12] we examined solvent effects on the UV absorption ([(*Z*)-**1f**]=5.0×10^{-5} mol dm^{-3}), fluorescence (5.0×10^{-5} mol dm^{-3}) and ^{13}C NMR (1.0×10^{-2} mol dm^{-3}) spectra of (*Z*)-**1f** in order to obtain evidence for the hydrogen-bonding solvation of this dehydronaphthylalanine derivative in the ground and excited singlet states (Table 6). The spectroscopic data obtained clearly show that the alteration in solvent from MeCN to MeOH causes a negligible shift of the first absorption band with an increase in its molar absorption coefficient, while in the latter solvent the fluorescence intensity is enhanced with no shift of the emission maximum. Because MeCN and MeOH have almost the same polarity (Table 6), these observations strongly suggest the occurrence of the hydrogen-bonding solvation of **1f** by the latter protic solvent in both the ground state and the excited singlet state. Interestingly, the amide carbonyl carbon signal of the starting **1f** was subject to a downfield shift (0.8–1.2 ppm) on changing the solvent from CD$_3$CN to CD$_3$OD, thus providing additional proof for the formation of hydrogen bonds in the ground state. It is, thus, very likely that the solvation of the excited singlet-state **1f** by MeOH accelerates the *Z*→*E* isomerization and then greatly enhances the electron-accepting ability of the naphthylmethylene moiety.

The fluorescence of (*Z*)-**1f** (5.0×10^{-5} mol dm^{-3}) was quenched by TEA (0.020–0.10 mol dm^{-3}; excitation wavelength, 283 nm) according to the equation, $I_0/I=1+2.8\pm0.2$[TEA], in MeCN. A comparison with the emission quenching in MeOH demonstrates that the quenching constant (4.5±0.5) in this protic solvent is larger than that in MeCN. If we are allowed to assume that the fluorescence lifetime of **1f** in the former solvent is not much different from that in the latter,[8] the result shown above (in addition to the fact that MeOH forms a hydrogen bond to TEA to lower the effective concentration of this amine) substantiates the enhanced electron-accepting ability of the excited singlet-state **1f** in MeOH.

Table 6. Solvent effects on the spectroscopic parameters of (*Z*)-**1f** at room temperature

Solvent	UV		Fluorescence		^{13}C NMR
	λ_{max}[a] (nm)	ϵ_{max}[b] (dm^3 mol^{-1} cm^{-1})	$\lambda_{f,max}$[c] (nm)	$I_{f,max}$[d]	δ(–CONH–) (ppm)
MeCN (35.94)[e]	309	12 300	373 (λ_{ex}=280 nm)[f]	25.1	
MeOH (32.66)[e]	309	13 300	373 (λ_{ex}=280 nm)[f]	37.4	
CD$_3$CN					165.6, 170.8
CD$_3$OD					166.4, 172.0

[a] UV absorption maximum.
[b] Molar absorption coefficient.
[c] Fluorescence maximum.
[d] Fluorescence intensity.
[e] Relative permittivity at 25°C (see Ref. 15).
[f] Excitation wavelength.

3. Conclusions

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 derivative **2** obtained is photochemically very stable, we were led to conclude that the photoreaction of substituted α-dehydro(1-naphthyl)alanine having an *N*-alkyl group (that is not so much bulky) in MeOH containing TEA presents a new method for constructing the dihydrobenzoquinolinone skeleton. We were also able to obtain significant information regarding the mechanism for the ET-initiated photocyclization reaction of **1**, through analyses of the product compositions (derived from the starting (*Z*)-**1**, (*E*)-**1f** and deuteriated (*Z*)-**1a**,**f**), as well as of substituent and solvent effects on both the photoreactivities of **1** and the selectivities of the products **2**–**4**.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR and IR spectra were taken with a JEOL JNM-A500 spectrometer and a Hitachi 270-30 infrared spectrometer, 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*)-**1** at room temperature were measured in the presence and absence of TEA under nitrogen with a Shimadzu RF-5000 spectrofluorimeter. Elemental analyses were performed on a Perkin–Elmer PE2400 series II CHNS/O analyzer. MeOH and MeCN were purified according to the standard procedures and freshly distilled prior to use.[15] TEA was fractionally distilled from sodium hydroxide. 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.

4.2. General procedure for the synthesis of (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone

N-Acetylglycine (30.0 g, 0.26 mol), 1-naphthaldehyde (48.4 g, 0.31 mol) and sodium acetate (16.0 g, 0.20 mol) were added to acetic anhydride (150 mL) and the resulting mixture was heated at 80–85°C for 6–7 h 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 EtOH and then with dry hexane. After the crude product had been air-dried at room temperature, it was recrystallized from hexane–$CHCl_3$ to give yellow crystals (24.4 g, 40%). Mp 159.0–160.0°C. 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). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.8, 122.8, 125.7, 126.3, 127.1, 127.4, 128.9, 129.1, 131.4, 131.8, 132.3, 133.3, 133.6, 166.8, 167.8.

4.3. General procedure for the synthesis of (*Z*)-2-acetylamino-3-(1-naphthyl)-2-propenamide [(*Z*)-1a], (*Z*)-2-acetylamino-*N*-alkyl-3-(1-naphthyl)-2-propenamides [(*Z*)-1b–j] and (*Z*)-2-acetylamino-3-(1-naphthyl)-*N*-phenyl-2-propenamide [(*Z*)-1k]

(*Z*)-2-Methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (0.020 mol) was added to dry $CHCl_3$ (200 mL) containing primary amine (0.021 mol) and the resulting solution was refluxed for 0.5–1.5 h. The reaction mixture was concentrated to dryness and the resulting residue was dissolved in EtOH (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 EtOH–hexane affording colorless crystals (40–60%).

4.3.1. (*Z*)-2-Acetylamino-3-(1-naphthyl)-2-propenamide [(*Z*)-1a]. Mp 192.0–194.0°C. IR (KBr): 3364, 3264, 3210, 1647, 1610 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.84 (3H, s,), 7.24 (1H, s), 7.51–7.59 (6H, m), 7.90 (1H, d, *J*=8.2 Hz), 7.94–7.99 (2H, m), 9.22 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 124.1, 124.3, 125.4, 125.9, 126.2, 126.3, 128.3, 128.4, 131.0, 131.3, 132.4, 133.1, 166.5, 169.3. Anal. calcd (found) for $C_{15}H_{14}N_2O_2$: C, 70.85 (70.82); H, 5.55 (5.17); N, 11.02% (10.91%).

4.3.2. (*Z*)-2-Acetylamino-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1b]. Mp 190.0–190.5°C. IR (KBr): 3340, 3236, 3180, 1644, 1628 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.84 (3H, s), 2.72 (3H, d, *J*=4.6 Hz), 7.51–7.58 (5H, m), 7.90 (1H, d, *J*=8.3 Hz), 7.94–7.98 (2H, m), 8.04 (1H, q, *J*=4.6 Hz), 9.24 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.7, 26.2, 124.16, 124.23, 125.5, 126.0, 126.2, 126.3, 128.3, 128.4, 131.1, 131.3, 132.5, 133.2, 165.2, 169.5. Anal. calcd (found) for $C_{16}H_{16}N_2O_2$: C, 71.62 (71.49); H, 6.01 (5.73); N, 10.44% (10.31%).

4.3.3. (*Z*)-2-Acetylamino-*N*-ethyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1c]. Mp 182.0–183.0°C. IR (KBr): 3310, 3240, 3180, 1656, 1623 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.10 (3H, t, *J*=7.3 Hz), 1.84 (3H, s), 3.22 (2H, dt, *J*=7.3, 7.3 Hz), 7.49 (1H, s), 7.50–7.58 (4H, m), 7.90 (1H, d, *J*=7.9 Hz), 7.94–7.98 (2H, m), 8.10 (1H, t, *J*=7.3 Hz), 9.22 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 14.7, 22.7, 34.0, 123.9, 124.2, 125.4, 126.0, 126.2, 126.3, 128.3, 128.4, 131.0, 131.4, 132.7, 133.2, 164.5, 169.4. Anal. calcd (found) for $C_{17}H_{18}N_2O_2$: C, 72.32 (71.97); H, 6.43 (6.30); N, 9.92% (9.83%).

4.3.4. (*Z*)-2-Acetylamino-3-(1-naphthyl)-*N*-propyl-2-propenamide [(*Z*)-1d]. Mp 170.0–171.0°C. IR (KBr): 3304, 3240, 3160, 1650, 1628 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.90 (3H, t, *J*=7.3 Hz), 1.51 (2H, m), 1.84 (3H, s), 3.13–3.18 (2H, m), 7.48 (1H, s), 7.51–7.59 (4H, m), 7.90 (1H, d, *J*=7.9 Hz), 7.94–7.98 (2H, m), 8.08 (1H, t, *J*=6.7 Hz), 9.21 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.3, 22.3, 22.6, 40.8, 123.7, 124.1, 125.4, 125.9, 126.16, 126.24, 128.2, 128.4, 131.0, 131.3, 132.7, 133.1, 164.6, 169.3. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (73.01); H, 6.80 (6.57); N, 9.45% (9.44%).

4.3.5. (Z)-2-Acetylamino-*N*-isopropyl-3-(1-naphthyl)-2-propenamide [(Z)-1e]. Mp 201.5–202.5°C. IR (KBr): 3334, 3270, 3214, 3160, 1650, 1623 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.15 (6H, d, *J*=6.1 Hz), 1.83 (3H, s), 3.98–4.05 (1H, m), 7.39 (1H, s), 7.51–7.58 (4H, m), 7.85 (1H, d, *J*=7.9 Hz), 7.86 (1H, d, *J*=7.9 Hz), 7.89–7.98 (2H, m), 9.18 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.2 (2C), 22.7, 40.9, 123.1, 124.3, 125.5, 126.0, 126.3 (2C), 128.2, 128.4, 131.0, 131.5, 133.0, 133.2, 164.0, 169.2. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (72.84); H, 6.80 (6.48); N, 9.45% (9.50%).

4.3.6. (Z)-2-Acetylamino-*N*-butyl-3-(1-naphthyl)-2-propenamide [(Z)-1f]. Mp 187.0–188.5°C. 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 (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.54); H, 7.14 (7.02); N, 9.03% (9.13%).

4.3.7. (Z)-2-Acetylamino-*N*-benzyl-3-(1-naphthyl)-2-propenamide [(Z)-1g]. Mp 185.0–186.5°C. IR (KBr): 3280, 3230, 1650, 1630 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.86 (3H, s), 4.43 (2H, d, *J*=6.1 Hz), 7.24 (1H, dd, *J*=6.7, 7.3 Hz), 7.23–7.32 (4H, m), 7.52–7.62 (5H, m), 7.91 (1H, d, *J*=7.9 Hz), 7.91–7.95 (2H, m), 8.69 (1H, t, *J*=6.1 Hz), 9.31 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 42.5, 124.1, 124.4, 125.4, 126.0, 126.2, 126.3, 126.5, 127.0 (2C), 128.0 (2C), 128.4 (2C), 131.0, 131.2, 132.5, 133.1, 139.6, 164.8, 169.6. Anal. calcd (found) for $C_{22}H_{20}N_2O_2$: C, 76.72 (76.42); H, 5.85 (5.75); N, 8.13% (7.92%).

4.3.8. (Z)-2-Acetylamino-*N*-(4-methoxybenzyl)-3-(1-naphthyl)-2-propenamide [(Z)-1h]. Mp 175.5–177.5°C. IR (KBr): 3304, 3270, 1650, 1626 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.85 (3H, s), 3.74 (3H, s), 4.35 (2H, d, *J*=6.1 Hz), 6.89 (2H, d, *J*=8.6 Hz), 7.29 (2H, d, *J*=8.6 Hz), 7.51–7.57 (4H, m), 7.60 (1H, d, *J*=7.3 Hz), 7.91 (1H, d, *J*=7.9 Hz), 7.95–7.98 (2H, m), 8.62 (1H, t, *J*=6.1 Hz), 9.28 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 41.9, 55.0, 113.5 (3C), 124.1, 124.4, 125.4, 125.9, 126.2, 126.3, 128.4 (3C), 131.0, 131.3, 131.6, 132.5, 133.1, 158.0, 164.7, 169.5. Anal. calcd (found) for $C_{23}H_{22}N_2O_3$: C, 73.78 (73.65); H, 5.92 (5.72); N, 7.48% (7.35%).

4.3.9. (Z)-2-Acetylamino-3-(1-naphthyl)-*N*-[4-(trifluoromethyl)benzyl]-2-propenamide [(Z)-1i]. Mp 201.5–202.5°C. IR (KBr): 3298, 3208, 3150, 1647, 1629 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.87 (3H, s), 4.50 (2H, d, *J*=5.5 Hz), 7.60 (2H, d, *J*=7.9 Hz), 7.53–7.62 (5H, m), 7.70 (2H, d, *J*=7.9 Hz), 7.92 (1H, d, *J*=7.9 Hz), 7.95–7.99 (2H, m), 8.78 (1H, t, *J*=5.5 Hz), 9.35 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 42.3, 124.2, 124.4 (1C, q, *J*=272 Hz), 124.5, 125.0 (2C, q, *J*=4 Hz), 125.5, 126.0, 126.4 (2C), 127.3 (1C, q, *J*=31 Hz), 127.8 (2C), 128.4 (2C), 131.0, 131.2, 132.5, 133.2, 144.7, 165.1, 169.8. Anal. calcd (found) for $C_{23}H_{19}F_3N_2O_2$: C, 66.98 (66.89); H, 4.64 (4.21); N, 6.79% (6.83%).

4.3.10. (Z)-2-Acetylamino-*N*-(*tert*-butyl)-3-(1-naphthyl)-2-propenamide [(Z)-1j]. Mp 181.0–182.0°C. IR (KBr): 3250, 1647, 1625 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.36 (9H, s), 1.82 (3H, s), 7.32 (1H, s), 7.37 (1H, s), 7.50–7.57 (4H, m), 7.89 (1H, d, *J*=7.9 Hz), 7.93–7.98 (2H, m), 9.18 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 28.5 (3C), 50.5, 122.6, 124.4, 125.5, 126.0, 126.2 (2C), 128.1, 128.4, 131.0, 131.6, 133.2, 133.5, 164.5, 169.0. Anal. calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.51); H, 7.14 (6.97); N, 9.03% (9.00%).

4.3.11. (Z)-2-Acetylamino-3-(1-naphthyl)-*N*-phenyl-2-propenamide [(Z)-1k]. Mp 214.0–214.5°C. IR (KBr): 3256, 1659, 1640 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.89 (3H, s), 7.09 (1H, dd, *J*=7.3, 7.6 Hz), 7.34 (2H, dd, *J*=7.6, 8.2 Hz), 7.42 (1H, s), 7.54–7.58 (3H, m), 7.67 (1H, d, *J*=7.3 Hz), 7.76 (2H, d, *J*=7.6 Hz), 7.93 (1H, d, *J*=8.2 Hz), 7.96–7.99 (1H, m), 8.04–8.06 (1H, m), 9.44 (1H, s), 10.08 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 120.1 (2C), 122.9, 123.4, 124.4, 125.5, 126.1, 126.4, 126.7, 128.5 (2C), 131.0, 131.2, 133.3, 133.4, 139.3, 164.0, 169.5. Anal. calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.14); H, 5.49 (5.39); N, 8.48% (8.61%).

4.4. General procedure for the irradiation of (*Z*)-1a–k

In order to examine the irradiation time dependence of the product distribution and composition, a MeOH solution (45 mL) of (*Z*)-**1** (3.75×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}), placed in a Pyrex vessel, was irradiated under nitrogen at room temperature 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** or (*Z*)-**1f** (3.75×10^{-3} mol dm^{-3}) was allowed to stand for 12 h in the presence of TEA (0.10 mol dm^{-3}) and then irradiated for 5.0 h with Pyrex-filtered light under an atmosphere of prepurified nitrogen. After 5.0 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 ^1H NMR analysis. The remaining solution of (*Z*)-**1a** was concentrated to dryness in vacuo and the resulting crystalline solid was washed several times with MeOH in order to obtain the analytical-grade deuteriated **2a** from the reaction mixture.

On the other hand, a solution (500 mL) of (*Z*)-**1a–k** (5.0×10^{-3} mol dm^{-3}) in MeOH containing TEA (0.10 mol dm^{-3}), 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 room temperature. After 1.5 h (**1a–i**) or 8 h (**1j,k**) 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 ^{1}H NMR analysis in DMSO-d_6. The remaining solutions of **1b–g** and **1i–k** were concentrated to dryness under reduced pressure and the resulting residues were subjected to column chromatography over silica gel (230 mesh, Merck) eluting with EtOAc–hexane. The crystalline residues derived from **1a** and **1h** were washed with small amounts of MeOH and then recrystallized from EtOH, allowing us to obtain analytical-grade **2a** and **2h**. The combined filtrates were concentrated to dryness and subjected to column chromatography in the same manner as above. For the purpose of isolating and purifying the photoproducts, preparative TLC plate (silica gel) was also used. Physical and spectroscopic properties of the isolated isomers [(*E*)-**1a–k**], 1,2-dihydrobenzo[*f*]quinolinones (**2a–i**), benzo[*f*]isoquinolines (**3a–k**) and 1-azetines (**4j**,**k**) are as follows.

4.4.1. (*E*)-1a. Mp 199.5–201.0°C. IR (KBr): 3334, 3250, 3166, 1653, 1610 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.03 (3H, s,), 7.16 (1H, br s), 7.28 (1H, br s), 7.42 (1H, s), 7.42 (1H, dd, J=6.7, 7.3 Hz), 7.49 (1H, d, J=6.7 Hz), 7.51–7.56 (2H, m), 7.80 (1H, d, J=7.9 Hz), 7.91 (1H, d, J=7.9 Hz), 7.99 (1H, d, J=7.9 Hz), 9.69 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.4, 112.8, 124.5, 125.3, 125.6, 125.7, 125.9, 127.0, 128.1, 131.2, 132.7, 133.0, 134.7, 166.2, 168.5. Anal. calcd (found) for $C_{15}H_{14}N_2O_2$: C, 70.85 (70.55); H, 5.55 (5.52); N, 11.02% (10.85%).

4.4.2. (*E*)-1b. Mp 167.5–168.5°C. IR (KBr): 3268, 1626, 1615 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.02 (3H, s), 2.43 (3H, d, J=4.9 Hz), 7.36 (1H, d, J=6.7 Hz), 7.42 (1H, dd, J=6.7, 7.3 Hz), 7.44 (1H, s), 7.53 (1H, dd, J=6.7, 7.3 Hz), 7.56 (1H, dd, J=6.7, 7.3 Hz), 7.78 (1H, q, J=4.9 Hz), 7.79 (1H, d, J=7.3 Hz), 7.91 (1H, d, J=7.3 Hz), 8.00 (1H, d, J=7.3 Hz), 9.75 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.5, 25.7, 112.9, 124.4, 125.2, 125.4, 125.8, 126.0, 127.1, 128.3, 131.2, 132.5, 133.1, 134.7, 165.1, 168.6. Anal. calcd (found) for $C_{16}H_{16}N_2O_2$: C, 71.62 (71.50); H, 6.01 (6.01); N, 10.44% (10.32%).

4.4.3. (*E*)-1c. Mp 157.0–158.0°C. IR (KBr): 3256, 1624, 1612 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.72 (3H, t, J=7.3 Hz), 2.02 (3H, s), 2.93 (2H, dq, J=6.5, 7.3 Hz), 7.40–7.41 (2H, m), 7.48 (1H, s), 7.52 (1H, dd, J=6.7, 6.7 Hz), 7.55 (1H, dd, J=6.7, 7.9 Hz), 7.77 (1H, t, J=6.5 Hz), 7.79–7.81 (1H, m), 7.91 (1H, d, J=6.7 Hz), 8.00 (1H, d, J=7.9 Hz), 9.71 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.6, 23.5, 33.3, 112.5, 124.5, 125.3, 125.6, 125.8, 125.9, 127.1, 128.2, 131.2, 132.5, 133.1, 135.1, 164.2, 168.6. Anal. calcd (found) for $C_{17}H_{18}N_2O_2$: C, 72.32 (72.61); H, 6.43 (6.41); N, 9.92% (10.21%).

4.4.4. (*E*)-1d. Mp 157.0–158.5°C. IR (KBr): 3252, 1630, 1620 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.53 (3H, t, J=7.3 Hz), 1.13 (2H, tq, J=6.7, 7.3 Hz), 2.02 (3H, s), 2.85 (2H, dt, J=6.1, 6.7 Hz), 7.39 (1H, dd, J=6.2, 7.3 Hz), 7.39 (1H, d, J=6.2 Hz), 7.46 (1H, s), 7.52 (1H, dd, J=6.7, 7.3 Hz), 7.55 (1H, dd, J=6.7, 7.9 Hz), 7.79 (1H, d, J=7.3 Hz), 7.80 (1H, t, J=6.1 Hz), 7.91 (1H, d, J=7.3 Hz), 8.00 (1H, d, J=7.9 Hz), 9.70 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.2, 21.4, 23.5, 40.5, 112.5, 124.6, 125.3, 125.6, 125.8, 125.9, 127.1, 128.2, 131.2, 132.6, 133.1, 135.1, 164.4, 168.5. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (73.14); H, 6.80 (6.83); N, 9.45% (9.20%).

4.4.5. (*E*)-1e. Mp 185.0–186.0°C. IR (KBr): 3274, 1639, 1629 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.77 (6H, d, J=6.7 Hz), 2.03 (3H, s), 3.77 (1H, dq, J=6.7, 7.9 Hz), 7.39 (1H, dd, J=7.3, 7.9 Hz), 7.42 (1H, d, J=7.3 Hz), 7.50 (1H, s), 7.53 (1H, dd, J=7.3, 7.7 Hz), 7.55 (1H, dd, J=7.7, 7.9 Hz), 7.59 (1H, d, J=7.9 Hz), 7.79 (1H, d, J=7.3 Hz), 7.90 (1H, d, J=7.9 Hz), 8.00 (1H, d, J=7.9 Hz), 9.68 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 21.4 (2C), 23.5, 40.2, 112.0, 124.5, 125.1, 125.5, 125.7, 125.8, 127.0, 128.1, 131.2, 132.4, 133.0, 135.1, 163.3, 168.5. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (72.53); H, 6.80 (6.66); N, 9.45% (9.45%).

4.4.6. (*E*)-1f. Mp 148.0–149.0°C. 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. EI-MS: *m*/*z* (%) 310 (M$^+$, 13.62). Anal. calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.29); H, 7.14 (7.19); N, 9.03% (9.14%).

4.4.7. (*E*)-1g. Mp 152.0–153.0°C. IR (KBr): 3280, 1690, 1680 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.04 (3H, s), 4.13 (2H, d, J=6.1 Hz), 6.90 (2H, d, J=7.3 Hz), 7.12–7.13 (3H, m), 7.29 (1H, dd, J=7.3, 7.9 Hz), 7.34 (1H, d, J=7.3 Hz), 7.41 (1H, s), 7.51–7.55 (2H, m), 7.80 (1H, d, J=7.9 Hz), 7.92 (1H, d, J=6.8 Hz), 8.00 (1H, d, J=6.9 Hz), 8.37 (1H, t, J=6.1 Hz), 9.80 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.3, 42.1, 113.1, 124.6, 125.3, 125.67, 125.74, 125.9, 126.3, 127.0, 127.1 (2C), 127.8 (2C), 128.1, 131.2, 132.4, 133.0, 134.8, 138.6, 164.6, 168.4. Anal. calcd (found) for $C_{22}H_{20}N_2O_2$: C, 76.72 (76.77); H, 5.85 (5.87); N, 8.13% (8.10%).

4.4.8. (*E*)-1h. Mp 131.0–131.5°C. IR (KBr): 3292, 1636, 1626 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.03 (3H, s), 3.70 (3H, s), 4.07 (2H, d, J=6.1 Hz), 6.69 (2H, d, J=8.5 Hz), 6.85 (2H, d, J=8.5 Hz), 7.29 (1H, dd, J=6.7, 7.9 Hz), 7.33 (1H, d, J=6.7 Hz), 7.41 (1H, s), 7.51–7.55 (2H, m), 7.80 (1H, d, J=7.9 Hz), 7.92 (1H, d, J=6.7 Hz), 8.00 (1H, d, J=6.7 Hz), 8.29 (1H, t, J=6.1 Hz), 9.78 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.4, 41.7, 55.0, 113.3 (3C), 124.6, 125.4, 125.7, 125.8, 125.9, 127.1, 128.2, 128.5 (2C), 130.5, 131.3, 132.4, 133.1, 134.8, 158.0, 164.5, 168.5. Anal. calcd (found) for $C_{23}H_{22}N_2O_3$: C, 73.78 (73.72); H, 5.92 (5.91); N, 7.48% (7.31%).

4.4.9. (*E*)-1i. Mp 158.0–159.0°C. IR (KBr): 3286, 1640, 1632 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.04 (3H, s), 4.20 (2H, d, J=6.1 Hz), 7.13 (2H, d, J=8.6 Hz), 7.28 (1H, dd, J=7.3, 7.9 Hz), 7.31 (1H, d, J=7.3 Hz), 7.35 (1H, s), 7.46 (2H, d, J=8.6 Hz), 7.51–7.56 (2H, m), 7.80

(1H, d, J=7.9 Hz), 7.92 (1H, d, J=7.6 Hz), 8.01 (1H, d, J=7.3 Hz), 8.44 (1H, t, J=6.1 Hz), 9.86 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.2, 41.8, 113.5, 124.3 (1C, q, J=271 Hz), 124.6 (2C, q, J=4 Hz), 125.3, 125.7, 125.8, 125.9, 127.10, 127.11 (1C, q, J=31 Hz), 127.8 (3C), 128.1, 131.2, 132.3, 133.0, 134.7, 143.7, 164.8, 168.4. Anal. calcd (found) for $C_{23}H_{19}F_3N_2O_2$: C, 66.98 (66.87); H, 4.64 (4.50); N, 6.79% (6.64%).

4.4.10. (*E*)-1j. Mp 137.0–138.0°C. IR (KBr): 3280, 1660, 1624 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.95 (9H, s), 2.04 (3H, s), 6.98 (1H, s), 7.42 (1H, dd, J=7.9, 7.9 Hz), 7.45 (1H, s), 7.46 (1H, d, J=7.9 Hz), 7.52 (1H, dd, J=6.7, 7.0 Hz), 7.54 (1H, dd, J=7.0, 7.0 Hz), 7.81 (1H, d, J=7.9 Hz), 7.91 (1H, d, J=6.7 Hz), 7.99 (1H, d, J=7.0 Hz), 9.62 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.6, 27.8 (3C), 50.2, 112.2, 124.7, 125.3, 125.8, 125.9, 126.0, 127.1, 128.2, 131.3, 132.7, 133.1, 135.8, 163.6, 168.6. Anal. calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.54); H, 7.14 (7.10); N, 9.03% (9.04%).

4.4.11. (*E*)-1k. Mp 200.0–201.0°C. IR (KBr): 3272, 1656, 1640 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.05 (3H, s), 6.99 (1H, dd, J=7.3, 7.3 Hz), 7.21 (2H, dd, J=7.3, 7.3 Hz), 7.34 (1H, dd, J=7.0, 8.2 Hz), 7.39 (2H, d, J=7.3 Hz), 7.40 (1H, s), 7.47 (1H, d, J=7.0 Hz), 7.53 (1H, dd, J=7.9, 8.2 Hz), 7.58 (1H, dd, J=7.9, 8.9 Hz), 7.75 (1H, d, J=8.2 Hz), 7.90 (1H, d, J=8.2 Hz), 8.07 (1H, d, J=8.9 Hz), 10.00 (1H, s), 10.01 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.3, 113.2, 119.8 (2C), 123.4, 124.5, 125.35, 125.39, 125.9, 126.0, 127.3, 128.3, 128.4 (2C), 131.2, 132.1, 133.1, 134.9, 138.8, 163.2, 168.4. Anal. calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.08); H, 5.49 (5.62); N, 8.48% (8.24%).

4.4.12. 2-Acetylamino-1,2-dihydro-3(1*H*)-benzo[*f*]quinolinone (2a). Mp 305.0–306.0°C. IR (KBr): 3316, 3204, 1690, 1628 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.95 (3H, s), 2.99 (1H, dd, J=14.6, 15.8 Hz), 3.64 (1H, dd, J=6.7, 15.8 Hz), 4.61 (1H, ddd, J=6.7, 7.9, 14.6 Hz), 7.16 (1H, d, J=8.6 Hz), 7.39 (1H, dd, J=7.0, 7.9 Hz), 7.52 (1H, dd, J=7.0, 8.6 Hz), 7.79 (1H, d, J=8.6 Hz), 7.85 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=8.6 Hz), 8.32 (1H, d, J=7.9 Hz), 10.45 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.7, 27.5, 47.6, 114.6, 116.7, 122.7, 124.0, 127.0, 128.1, 128.5, 129.6, 131.1, 135.0, 168.7, 169.5. Anal. calcd (found) for $C_{15}H_{14}N_2O_2$: C, 70.85 (70.55); H, 5.55 (5.53); N, 11.02% (10.69%).

4.4.13. 2-Acetylamino-2-deutero-1-hydro-3(1*H*)-benzo[*f*]-quinolinone (deuteriated 2a). Mp 305.0–306.0°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.94 (3H, s), 2.99 (1H, d, J=15.9 Hz), 3.64 (1H, d, J=15.9 Hz), 7.16 (1H, d, J=8.6 Hz), 7.39 (1H, dd, J=7.3, 7.9 Hz), 7.52 (1H, dd, J=7.3, 8.6 Hz), 7.79 (1H, d, J=8.6 Hz), 7.85 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=8.6 Hz), 8.30 (1H, s), 10.45 (1H, s).

4.4.14. 2-Acetylamino-1,2-dihydro-4-methyl-3(1*H*)-benzo-[*f*]quinolinone (2b). Mp 231.5–232.5°C. IR (KBr): 3320, 1672, 1634 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.95 (3H, s), 3.01 (1H, dd, J=14.7, 15.7 Hz), 3.41 (3H, s), 3.65 (1H, dd, J=6.1, 15.7 Hz), 4.57 (1H, ddd, J=6.1, 7.9, 14.7 Hz), 7.45 (1H, dd, J=7.0, 7.9 Hz), 7.49 (1H, d, J=8.9 Hz), 7.56 (1H, dd, J=7.0, 7.9 Hz), 7.91 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=8.9 Hz), 8.01 (1H, d, J=7.9 Hz), 8.34 (1H, d, J=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 26.8, 30.3, 48.0, 116.1, 117.6, 123.0, 124.5, 127.0, 128.0, 128.3, 129.6, 130.5, 137.1, 168.2, 169.3. Anal. calcd (found) for $C_{16}H_{16}N_2O_2$: C, 71.62 (71.52); H, 6.01 (5.86); N, 10.44% (10.41%).

4.4.15. 2-Acetylamino-4-ethyl-1,2-dihydro-3(1*H*)-benzo-[*f*]quinolinone (2c). Mp 221.0–222.0°C. IR (KBr): 3296, 1666, 1634 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.18 (3H, t, J=7.0 Hz), 1.95 (3H, s), 2.97 (1H, dd, J=14.7, 15.6 Hz), 3.64 (1H, dd, J=6.1, 15.6 Hz), 4.05 (2H, q, J=7.0 Hz), 4.57 (1H, ddd, J=6.1, 7.6, 14.7 Hz), 7.45 (1H, dd, J=7.0, 7.3 Hz), 7.51 (1H, d, J=8.9 Hz), 7.56 (1H, dd, J=7.3, 7.9 Hz), 7.91 (1H, d, J=7.0 Hz), 7.93 (1H, d, J=8.9 Hz), 8.00 (1H, d, J=7.9 Hz), 8.34 (1H, d, J=7.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.1, 22.6, 27.0, 37.6, 48.0, 116.0, 118.1, 123.0, 124.6, 127.0, 128.2, 128.3, 129.6, 130.8, 136.0, 167.9, 169.3. Anal. calcd (found) for $C_{17}H_{18}N_2O_2$: C, 72.32 (71.94); H, 6.43 (6.22); N, 9.92% (9.73%).

4.4.16. 2-Acetylamino-1,2-dihydro-4-propyl-3(1*H*)-benzo-[*f*]quinolinone (2d). Mp 192.5–193.5°C. IR (KBr): 3304, 1668, 1640 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.88 (3H, t, J=7.3 Hz), 1.51–1.64 (2H, m), 1.95 (3H, s), 2.97 (1H, dd, J=15.0, 15.6 Hz), 3.65 (1H, dd, J=6.1, 15.6 Hz), 3.93–4.09 (2H, m), 4.57 (1H, ddd, J=6.1, 7.9, 15.0 Hz), 7.45 (1H, dd, J=7.3, 7.9 Hz), 7.51 (1H, d, J=8.9 Hz), 7.56 (1H, dd, J=7.3, 7.9 Hz), 7.91 (1H, d, J=7.9 Hz), 7.91 (1H, d, J=8.9 Hz), 8.00 (1H, d, J=7.9 Hz), 8.36 (1H, d, J=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.0, 20.5, 22.7, 27.0, 43.5, 48.1, 116.3, 118.2, 123.1, 124.6, 127.1, 128.1, 128.3, 129.6, 130.8, 136.0, 168.3, 169.4. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (72.65); H, 6.80 (6.75); N, 9.45% (9.43%).

4.4.17. 2-Acetylamino-1,2-dihydro-4-isopropyl-3(1*H*)-benzo[*f*]quinolinone (2e). Mp 163.5–164.0°C. IR (KBr): 3356, 1668 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.47 (3H, d, J=6.7 Hz), 1.52 (3H, d, J=7.3 Hz), 1.93 (3H, s), 2.92 (1H, dd, J=14.7, 15.3 Hz), 3.55 (1H, dd, J=5.5, 15.3 Hz), 4.37 (1H, ddd, J=5.5, 7.9, 14.7 Hz), 4.62 (1H, qq, J=6.7, 7.3 Hz), 7.44 (1H, dd, J=7.3, 7.9 Hz), 7.52 (1H, d, J=8.6 Hz), 7.54 (1H, dd, J=7.3, 7.9 Hz), 7.88 (1H, d, J=8.6 Hz), 7.89 (1H, d, J=7.9 Hz), 7.99 (1H, d, J=7.9 Hz), 8.28 (1H, d, J=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 19.5, 20.9, 22.6, 27.0, 49.0, 49.6, 117.5, 120.1, 123.2, 124.7, 127.0, 127.7, 128.2, 129.7, 130.6, 137.0, 168.7, 169.4. Anal. calcd (found) for $C_{18}H_{20}N_2O_2$: C, 72.95 (72.61); H, 6.80 (6.71); N, 9.45% (9.33%).

4.4.18. 2-Acetylamino-4-butyl-1,2-dihydro-3(1*H*)-benzo-[*f*]quinolinone (2f). Mp 157.0–158.0°C. IR (KBr): 3308, 1668, 1642 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.89 (3H, t, J=7.3 Hz), 1.31 (2H, tq, J=7.3, 7.6 Hz), 1.50–1.57 (2H, m), 1.95 (3H, s), 2.96 (1H, dd, J=14.6, 15.3 Hz), 3.64 (1H, dd, J=6.1, 15.3 Hz), 3.95–4.14 (2H, m), 4.56 (1H, ddd, J=6.1, 7.9, 14.6 Hz), 7.45 (1H, dd, J=7.6, 7.9 Hz), 7.51 (1H, d, J=8.2 Hz), 7.55 (1H, dd, J=7.6, 8.2 Hz), 7.91

(1H, d, *J*=8.5 Hz), 7.92 (1H, d, *J*=8.5 Hz), 8.00 (1H, d, *J*=8.2 Hz), 8.34 (1H, d, *J*=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.7, 19.4, 22.6, 27.0, 29.4, 41.7, 48.1, 116.2, 118.2, 123.1, 124.6, 127.1, 128.1, 128.3, 129.6, 130.8, 136.0, 168.2, 169.4. EI-MS: *m*/*z* (%) 310 (M^+, 0.57). Anal. calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.14); H, 7.14 (7.13); N, 9.03% (9.11%).

4.4.19. 2-Acetylamino-4-benzyl-1,2-dihydro-3(1*H*)-benzo-[*f*]quinolinone (2g). Mp 256.0–257.0°C. IR (KBr): 3310, 1674, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.97 (3H, s), 3.10 (1H, dd, *J*=14.7, 15.7 Hz), 3.73 (1H, dd, *J*=6.4, 15.7 Hz), 4.78 (1H, ddd, *J*=6.4, 7.9, 14.7 Hz), 5.31 (2H, s), 7.21 (1H, dd, *J*=7.0, 7.0 Hz), 7.26–7.32 (4H, m), 7.35 (1H, d, *J*=8.9 Hz), 7.43 (1H, dd, *J*=7.6, 8.2 Hz), 7.55 (1H, dd, *J*=7.6, 8.2 Hz), 7.78 (1H, d, *J*=8.9 Hz), 7.84 (1H, d, *J*=8.2 Hz), 8.02 (1H, d, *J*=8.2 Hz), 8.45 (1H, d, *J*=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 27.0, 45.4, 48.0, 116.4, 118.1, 123.1, 124.6, 126.4 (2C), 126.9, 127.0, 127.9, 128.2, 128.5 (2C), 129.6, 130.6, 136.1, 137.1, 168.7, 169.3. Anal. calcd (found) for $C_{22}H_{20}N_2O_2$: C, 76.72 (77.02); H, 5.85 (5.79); N, 8.13% (8.09%).

4.4.20. 2-Acetylamino-1,2-dihydro-4-(4-methoxybenzyl)-3(1*H*)-benzo[*f*]quinolinone (2h). Mp 238.0–239.0°C. IR (KBr): 3296, 1668, 1638 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s), 3.06 (1H, dd, *J*=14.7, 15.9 Hz), 3.68 (3H, s), 3.71 (1H, dd, *J*=6.7, 15.9 Hz), 4.74 (1H, ddd, *J*=6.7, 7.9, 14.7 Hz), 5.21 (1H, d, *J*=15.9 Hz), 5.27 (1H, d, *J*=15.9 Hz), 6.85 (2H, d, *J*=8.6 Hz), 7.20 (2H, d, *J*=8.6 Hz), 7.39 (1H, d, *J*=8.6 Hz), 7.43 (1H, dd, *J*=7.3, 7.9 Hz), 7.55 (1H, dd, *J*=7.3, 7.9 Hz), 7.79 (1H, d, *J*=8.6 Hz), 7.84 (1H, d, *J*=7.9 Hz), 8.01 (1H, d, *J*=7.9 Hz), 8.44 (1H, d, *J*=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.7, 27.0, 44.8, 48.1, 54.0, 114.0 (2C), 116.6, 118.3, 123.1, 124.7, 127.1, 127.9 (3C), 128.3, 129.0, 129.6, 130.7, 136.1, 158.3, 168.7, 169.4. Anal. calcd (found) for $C_{23}H_{22}N_2O_3$: C, 73.78 (73.52); H, 5.92 (5.84); N, 7.48% (7.42%).

4.4.21. 2-Acetylamino-1,2-dihydro-4-[4-(trifluoromethyl)-benzyl]-3(1*H*)-benzo[*f*]quinolinone (2i). Mp 233.0–234.0°C. IR (KBr): 3334, 1680, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s), 3.14 (1H, dd, *J*=14.6, 15.3 Hz), 3.75 (1H, dd, *J*=6.7, 15.3 Hz), 4.81 (1H, ddd, *J*=6.7, 7.9, 14.6 Hz), 5.37 (1H, d, *J*=17.1 Hz), 5.43 (1H, d, *J*=17.1 Hz), 7.32 (1H, d, *J*=9.2 Hz), 7.44 (1H, dd, *J*=7.3, 7.9 Hz), 7.50 (2H, d, *J*=7.9 Hz), 7.57 (1H, dd, *J*=7.3, 7.9 Hz), 7.68 (2H, d, *J*=7.9 Hz), 7.80 (1H, d, *J*=9.2 Hz), 7.85 (1H, d, *J*=7.9 Hz), 8.04 (1H, d, *J*=7.9 Hz), 8.45 (1H, d, *J*=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 26.9, 45.2, 47.9, 116.1, 118.2, 123.1, 124.1 (1C, q, *J*=273 Hz), 124.7, 125.4 (2C, q, *J*=4 Hz), 127.1, 127.2 (2C), 127.6 (1C, q, *J*=31 Hz), 128.0, 128.2, 129.6, 130.6, 135.8, 142.1, 168.8, 169.3. Anal. calcd (found) for $C_{23}H_{19}F_3N_2O_2$: C, 66.98 (66.87); H, 4.64 (4.65); N, 6.79% (6.60%).

4.4.22. 2-Aminocarbonyl-4-methylbenzo[*f*]isoquinoline (3a). Mp 254.0–255.5°C. IR (KBr): 3442, 1683 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.03 (3H, s), 7.76 (1H, br s), 7.83–7.84 (2H, m), 8.12 (1H, d, *J*=9.2 Hz), 8.12–8.14 (1H, m), 8.17 (1H, d, *J*=9.2 Hz), 8.27 (1H, br s), 8.92–8.94 (1H, m), 9.16 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 113.3, 122.8, 123.8, 126.3, 128.0, 128.7, 128.8, 129.1, 129.7, 132.9, 134.6, 144.6, 157.1, 166.5. Anal. calcd (found) for $C_{15}H_{12}N_2O$: C, 76.25 (75.96); H, 5.12 (5.02); N, 11.86% (11.79%).

4.4.23. 2-(Methylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3b). Mp 135.0–136.0°C. IR (KBr): 3406, 1659 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.94 (3H, d, *J*=4.9 Hz), 3.03 (3H, s), 7.81–7.85 (2H, m), 8.11 (1H, d, *J*=9.2 Hz), 8.12–8.14 (1H, m), 8.16 (1H, d, *J*=9.2 Hz), 8.84 (1H, q, *J*=4.9 Hz), 8.91–8.93 (1H, m), 9.11 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 26.0, 112.8, 122.7, 123.8, 126.1, 127.9, 128.6, 128.7, 129.0, 129.5, 132.8, 134.5, 144.3, 157.0, 164.7. Anal. calcd (found) for $C_{16}H_{14}N_2O$: C, 76.78 (76.69); H, 5.64 (5.71); N, 11.19% (11.37%).

4.4.24. 2-(Ethylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3c). Mp 104.0–105.0°C. IR (KBr): 3394, 1659 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.21 (3H, t, *J*=7.0 Hz), 3.04 (3H, s), 3.44 (2H, dq, *J*=6.8, 7.0 Hz), 7.82–7.84 (2H, m), 8.12 (1H, d, *J*=9.2 Hz), 8.12–8.14 (1H, m), 8.18 (1H, d, *J*=9.2 Hz), 8.88 (1H, t, *J*=6.8 Hz), 8.91–8.93 (1H, m), 9.13 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.0, 22.5, 33.8, 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, 163.8. Anal. calcd (found) for $C_{17}H_{16}N_2O$: C, 77.25 (76.98); H, 6.10 (6.04); N, 10.60% (10.49%).

4.4.25. 4-Methyl-2-(propylaminocarbonyl)benzo[*f*]isoquinoline (3d). Mp 97.0–98.0°C. IR (KBr): 3394, 1680 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.94 (3H, t, *J*=7.3 Hz), 1.63 (2H, tq, *J*=7.3, 7.3 Hz), 3.04 (3H, s), 3.38 (2H, dt, *J*=6.1, 7.3 Hz), 7.82–7.85 (2H, m), 8.11 (1H, d, *J*=8.5 Hz), 8.10–8.13 (1H, m), 8.16 (1H, d, *J*=8.5 Hz), 8.86 (1H, t, *J*=6.1 Hz), 8.90–8.91 (1H, m), 9.12 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.4, 22.59, 22.64, 40.7, 113.0, 122.8, 123.8, 126.3, 127.9, 128.67, 128.73, 129.1, 129.6, 132.9, 134.6, 144.4, 157.1, 164.2. Anal. calcd (found) for $C_{18}H_{18}N_2O$: C, 77.67 (77.66); H, 6.52 (6.47); N, 10.06% (10.34%).

4.4.26. 2-(Isopropylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3e). Mp 160.5–161.0°C. IR (KBr): 3370, 1668 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (6H, d, *J*=6.1 Hz), 3.04 (3H, s), 4.23 (1H, dq, *J*=6.1, 8.6 Hz), 7.81–7.85 (2H, m), 8.12 (1H, d, *J*=9.2 Hz), 8.11–8.14 (1H, m), 8.17 (1H, d, *J*=9.2 Hz), 8.52 (1H, d, *J*=8.6 Hz), 8.90–8.93 (1H, m), 9.13 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.4 (2C), 22.5, 40.8, 113.0, 122.8, 123.8, 126.3, 127.9, 128.6, 128.7, 129.1, 129.6, 132.9, 134.6, 144.3, 157.1, 163.2. Anal. calcd (found) for $C_{18}H_{18}N_2O$: C, 77.67 (77.79); H, 6.52 (6.58); N, 10.06% (10.10%).

4.4.27. 2-(Butylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3f). Mp 61.5–62.5°C. 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. EI-MS: *m/z* (%) 292 (M^+, 8.94). Anal. calcd (found) for $C_{19}H_{20}N_2O$: C, 78.05 (77.85); H, 6.89 (7.09); N, 9.58% (9.74%).

4.4.28. 2-(Benzylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3g). Mp 147.0–148.0°C. IR (KBr): 3394, 1674 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.04 (3H, s), 4.62 (2H, d, *J*=6.4 Hz), 7.26 (1H, dd, *J*=7.3, 7.3 Hz), 7.34 (2H, dd, *J*=7.3, 7.6 Hz), 7.40 (2H, d, *J*=7.6 Hz), 7.81–7.85 (2H, m), 8.13–8.14 (1H, m), 8.14 (1H, d, *J*=8.9 Hz), 8.19 (1H, d, *J*=8.9 Hz), 8.93–8.95 (1H, m), 9.17 (1H, s), 9.39 (1H, t, *J*=6.4 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 42.4, 113.2, 122.7, 123.8, 126.3, 126.7, 127.4 (2C), 127.9, 128.2 (2C), 128.6, 128.7, 129.0, 129.6, 132.8, 134.5, 139.6, 144.2, 157.1, 164.2. Anal. calcd (found) for $C_{22}H_{18}N_2O$: C, 80.96 (81.05); H, 5.56 (5.47); N, 8.58% (8.70%).

4.4.29. 2-(4-Methoxybenzylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3h). Mp 142.0–143.0°C. IR (KBr): 3382, 1671 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.03 (3H, s), 3.73 (3H, s), 4.54 (2H, d, *J*=6.1 Hz), 6.91 (2H, d, *J*=8.5 Hz), 7.34 (2H, d, *J*=8.5 Hz), 7.82–7.85 (2H, m), 8.13 (1H, d, *J*=9.2 Hz), 8.12–8.15 (1H, m), 8.17 (1H, d, *J*=9.2 Hz), 8.91–8.93 (1H, m), 9.16 (1H, s), 9.30 (1H, t, *J*=6.1 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 42.0, 55.1, 113.3, 113.7 (2C), 123.8, 126.4, 127.8, 128.7, 128.8, 128.9 (3C), 129.2, 129.7, 131.6, 132.9, 134.6, 144.3, 157.2, 158.3, 164.2. Anal. calcd (found) for $C_{23}H_{20}N_2O_2$: C, 77.51 (77.11); H, 5.66 (5.67); N, 7.86% (7.75%).

4.4.30. 4-Methyl-2-[4-(trifluoromethyl)benzylaminocarbonyl]benzo[*f*]isoquinoline (3i). Mp 149.0–149.5°C. IR (KBr): 3376, 1671 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.05 (3H, s), 4.70 (2H, d, *J*=6.1 Hz), 7.61 (2H, d, *J*=8.6 Hz), 7.71 (2H, d, *J*=8.6 Hz), 7.81–7.85 (2H, m), 8.13 (1H, d, *J*=9.2 Hz), 8.12–8.14 (1H, m), 8.18 (1H, d, *J*=9.2 Hz), 8.91–8.93 (1H, m), 9.16 (1H, s), 9.57 (1H, t, *J*=6.1 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 42.2, 113.3, 122.7, 123.8, 125.3 (1C, q, *J*=271 Hz), 125.1 (2C, q, *J*=4 Hz), 126.4, 127.4 (1C, q, *J*=33 Hz), 127.9, 128.0 (2C), 128.6, 128.7, 129.1, 129.7, 132.8, 134.5, 144.0, 144.6, 157.2, 164.6. Anal. calcd (found) for $C_{23}H_{17}F_3N_2O$: C, 70.04 (69.81); H, 4.34 (4.31); N, 7.10% (7.03%).

4.4.31. 2-(*tert*-Butylaminocarbonyl)-4-methylbenzo[*f*]isoquinoline (3j). Mp 211.5–212.5°C. IR (KBr): 3376, 1671 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.49 (9H, s), 3.03 (3H, s), 7.82–7.86 (2H, m), 8.13 (1H, d, *J*=9.2 Hz), 8.12–8.15 (1H, m), 8.19 (1H, d, *J*=9.2 Hz), 8.30 (1H, s), 8.92–8.94 (1H, m), 9.14 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.7, 28.5 (3C), 50.3, 112.6, 122.8, 123.8, 126.3, 128.0, 128.67, 128.74, 129.2, 129.6, 132.9, 134.7, 144.5, 157.0, 163.1. Anal. calcd (found) for $C_{19}H_{20}N_2O$: C, 78.05 (77.98); H, 6.89 (6.74); N, 9.58% (9.76%).

4.4.32. 2-Anilinocarbonyl-4-methylbenzo[*f*]isoquinoline (3k). Mp 212.0–213.0°C. IR (KBr): 3256, 1674 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.10 (3H, s), 7.15 (1H, dd, *J*=7.6, 7.6 Hz), 7.41 (2H, dd, *J*=7.6, 7.9 Hz), 7.82–7.86 (2H, m), 7.95 (2H, d, *J*=7.9 Hz), 8.13–8.14 (1H, m), 8.16 (1H, d, *J*=9.2 Hz), 8.21 (1H, d, *J*=9.2 Hz), 8.97–8.99 (1H, m), 9.25 (1H, s), 10.65 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 113.7, 120.1 (2C), 122.8, 123.9, 124.0, 126.6, 128.0, 128.6, 128.7 (3C), 129.2, 130.0, 132.9, 134.7, 138.3, 143.9, 157.3, 162.7. Anal. calcd (found) for $C_{21}H_{16}N_2O$: C, 80.75 (80.87); H, 5.16 (5.09); N, 8.97% (9.07%).

We succeeded in isolating small amounts of *cis*-**4j**, *trans*-**4j**, *cis*-**4k** and *trans*-**4k** whose ^{1}H and ^{13}C NMR spectra were consistent with the proposed structures, although the *cis*- and *trans*-isomers isolated, in most cases, were contaminated with the azetine-derived decomposition products.

4.4.33. *cis*-4-(*tert*-Butylaminocarbonyl)-2-methyl-3-(1-naphthyl)-1-azetine (*cis*-4j). White solid. IR (KBr): 3280, 1680, 1650 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.48 (9H, s), 2.15 (3H, d, *J*=1.2 Hz), 5.11 (1H, dd, *J*=1.2, 10.4 Hz), 6.46 (1H, d, *J*=10.4 Hz), 6.75 (1H, s), 7.42–7.45 (2H, m), 7.51 (1H, dd, *J*=6.1, 6.7 Hz), 7.53 (1H, dd, *J*=6.1, 6.7 Hz), 7.79–7.81 (1H, m), 7.89 (1H, d, *J*=6.7 Hz), 8.00 (1H, d, *J*=6.7 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.7, 27.3 (3C), 49.2, 72.9, 80.0, 123.5, 124.1, 124.9, 125.4, 125.6, 127.6, 128.1, 130.1, 132.8, 132.9, 165.6, 166.4.

4.4.34. *trans*-4-(*tert*-Butylaminocarbonyl)-2-methyl-3-(1-naphthyl)-1-azetine (*trans*-4j). Oily liquid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.30 (9H, s), 2.14 (3H, d, *J*=1.2 Hz), 4.31 (1H, dd, *J*=1.2, 7.0 Hz), 6.28 (1H, d, *J*=7.0 Hz), 7.49–7.59 (4H, m), 7.73 (1H, s), 7.78 (1H, d, *J*=7.9 Hz), 7.92 (1H, d, *J*=7.9 Hz), 8.00 (1H, d, *J*=7.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.5, 28.3 (3C), 50.4, 77.1, 80.2, 122.0, 122.8, 125.5, 126.0, 126.4, 128.2, 128.8, 129.2, 133.4, 135.9, 164.6, 169.3.

4.4.35. *cis*-4-Anilinocarbonyl-2-methyl-3-(1-naphthyl)-1-azetine (*cis*-4k). Mp 172.0–173.0°C. IR (KBr): 3350, 1695, 1660 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.22 (3H, s), 5.30 (1H, d, *J*=10.4 Hz), 6.63 (1H, d, *J*=10.4 Hz), 6.82 (2H, d, *J*=7.9 Hz), 6.87 (1H, dd, *J*=7.3, 7.3 Hz), 7.03 (2H, dd, *J*=7.3, 7.9 Hz), 7.42 (1H, dd, *J*=7.9, 7.9 Hz), 7.45 (1H, dd, *J*=7.3, 7.9 Hz), 7.52 (1H, dd, *J*=7.9, 8.5 Hz), 7.53 (1H, d, *J*=7.9 Hz), 7.77 (1H, d, *J*=7.9 Hz), 7.83 (1H, d, *J*=7.9 Hz), 8.06 (1H, d, *J*=8.5 Hz), 9.32 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.9, 73.6, 80.0, 120.1 (2C), 123.4, 123.5, 123.7, 124.9, 125.5, 125.9, 127.9, 128.1 (2C), 128.2, 129.9, 132.6, 132.7, 137.6, 166.5, 166.8. Anal. calcd (found) for $C_{21}H_{18}N_2O{\cdot}H_2O$: C, 75.88 (76.20); H, 6.06 (5.83); N, 8.43% (8.26%).

4.4.36. *trans*-4-Anilinocarbonyl-2-methyl-3-(1-naphthyl)-1-azetine (*trans*-4k). Oily liquid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.20 (3H, d, *J*=1.2 Hz), 4.61 (1H, dd, *J*=1.2, 7.0 Hz), 6.49 (1H, d, *J*=7.0 Hz), 7.11 (1H, dd, *J*=7.6, 7.6 Hz), 7.35 (2H, dd, *J*=7.6, 7.9 Hz), 7.52–7.58 (4H, m), 7.66 (2H, d, *J*=7.9 Hz), 7.85–7.87 (1H, m), 7.95–7.97 (1H, m), 8.01–8.03 (1H, m), 10.20 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 13.5, 77.2, 80.0, 119.6 (2C), 122.5, 122.6, 123.8, 125.5, 126.1, 126.7, 128.6, 128.8 (2C), 129.0, 129.2, 133.5, 135.4, 138.5, 165.5, 168.6.

4.5. Control experiments

A MeOH solution (100 mL) of (*Z*)-**1f** (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 (EtOAc–hexane). This procedure allowed us to isolate (*Z*)-**1f**, (*E*)-**1f**, **3f** and **5f** (major product). Physical and spectroscopic properties of **5f** are shown below.

On the other hand, we employed a ^{1}H NMR tube instead of a Pyrex vessel in order to investigate whether the concentration of TEA is changed during irradiation. A CD_3OD solution of (*Z*)-**1f** (2.5×10^{-2} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}) and 1,4-dioxane (0.10 mol dm^{-3}) was placed in a NMR tube and sealed after the solution was saturated with nitrogen. This sealed solution was irradiated for 4–8 h at room temperature with Pyrex-filtered light from a 450 W high-pressure Hg lamp and subjected to ^{1}H NMR analysis.

4.5.1. 2-Acetylamino-4-butyl-3(1*H*)-benzo[*f*]quinolinone (5f). Mp 163.0–164.0°C. 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. EI-MS: *m*/*z* (%) 308 (M$^+$, 14.90). Anal. calcd (found) for $C_{19}H_{20}N_2O_2$: C, 74.00 (73.55); H, 6.54 (6.37); N, 9.08% (8.90%).

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