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Highly selective conversion of *N*-aroyl-α-dehydronaphthylalaninamides into 3,4-dihydrobenzoquinolinone derivatives via photoinduced intermolecular electron transfer

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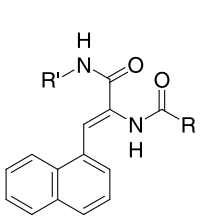
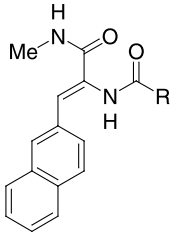
Abstract—The irradiation of substituted (*Z*)-*N*-aroyl-α-dehydronaphthylalaninamides [(*Z*)-**1**] in methanol containing triethylamine (TEA) with Pyrex-filtered light was found to give 3,4-dihydrobenzoquinolinone derivatives (**2**) in high yields along with minor amounts of 4,5-dihydrooxazole derivatives (**3**). Analysis of the substituent effects on product composition revealed that both the photoreactivity of **1** and the selectivity of **2** are decreased with increasing electron-withdrawing ability of the substituent introduced at the *para*-position on the *N*-benzoyl benzene ring. From the analysis of the dependence of the quantum yield for the formation of **2** on the TEA concentration, it was found that back electron transfer occurs efficiently within an (*E*)-**1** anion radical–TEA cation radical pair intermediate.

1. Introduction

Organic photochemistry has continued to contribute to the development of efficient and selective transformations for the preparation of complicated molecules which could not have been synthesized by conventional methods. In recent years much attention is being devoted to the synthetic application of photoinduced electron transfer (PET) reactions, owing to the fact that many of these reactions enable the construction of various heterocyclic rings.[1] On the other hand, α-dehydroamino acid derivative is one of the important intermediates for the synthesis of natural and biologically active products. Many useful synthetic methods of substituted α-dehydroamino acid derivatives have been reported but there have been only limited investigations of the photochemistry of these amino acid derivatives.[2,3] Taking into account the fact that aromatic olefins undergo efficient PET reactions in their excited states,[4] it can be expected that α-dehydroamino acids having the aromatic olefin chromophore are subject to PET reactions. Keeping this expectation in mind, we embarked on a systematic study toward the characterization of the excited-state reactivity of substituted α-dehydroamino acids.[5–7] In the course of this study we discovered a novel intermolecular ET-initiated photocyclization reaction of substituted *N*-acetyl-α-dehydronaphthylalaninamides that afford 3,4-dihydrobenzo[*f*]-quinolinones.[6] Because many heterocyclic compounds having a dihydroquinolinone ring exhibit pharmacological and physiological activities, it is of fundamental significance to develop synthetic methods for the construction of the quinolinone ring.[8] If we consider that PET reactions of



(*Z*)-**1a–i**



(*Z*)-**1j–l**

1a (R= Ph, R'= Me); **1b** (R= 4-OMeC$_6$H$_4$, R'= Me);
1c (R= 4-BrC$_6$H$_4$, R'= Me); **1d** (R= 4-CF$_3$C$_6$H$_4$, R'= Me);
1e (R= 4-CNC$_6$H$_4$, R'= Me); **1f** [R= 2,4-(OMe)$_2$C$_6$H$_3$, R'= Me];
1g (R= *t*-Bu, R'= Me); **1h** (R= Ph, R'= H); **1i** (R= Ph, R'= PhCH$_2$);
1j (R= Ph); **1k** (R= 4-OMeC$_6$H$_4$); **1l** [R= 2,4-(OMe)$_2$C$_6$H$_3$]

N-aroyl-α-dehydronaphthylalaninamides may afford the corresponding dihydrobenzoquinolinone derivatives in high selectivities, it is possible to extend synthetic utility of the ET-initiated photocyclization reactions described

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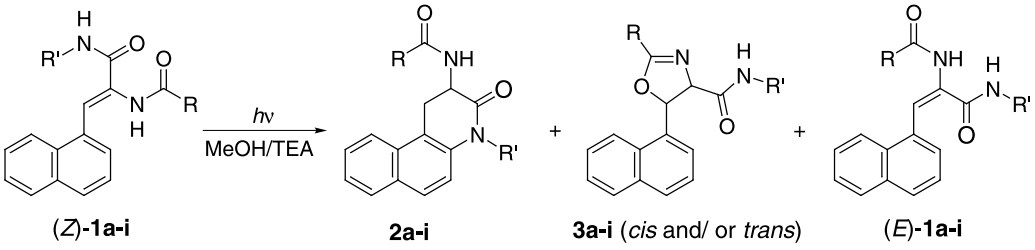
above. For this end we synthesized (*Z*)-*N*-aroyl-α-dehydronaphthylalaninamides [(*Z*)-**1a–l**] and investigated substituent effects on both the reactivity of (*Z*)-**1** and the selectivity of each photoproduct. Additionally, we analyzed quantum yield for the photoisomerization of (*E*)-**1** as well as the effects of TEA concentration on the quantum yield for the formation of dihydrobenzoquinolinone derivative, hoping to shed much light on the mechanism of novel ET-initiated photocyclization reactions.

2. Results and discussion

2.1. Photocyclization of (*Z*)-1a–l

The starting (*Z*)-isomers (**1a–l**) were prepared in good yields by the ring-opening reactions of (*Z*)-naphthyl-substituted oxazolones with primary amines.[9] After a nitrogen-saturated methanol solution of (*Z*)-**1a** (3.75×10^{-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 3 h at room temperature, the product mixture obtained was washed with a small amount of EtOH and then with hexane, giving the analytically pure 3,4-dihydrobenzo[*f*]quinolinone derivative (**2a**, 67%; conversion, >99%). Preparative TLC (silica gel) of the residual solid [that was obtained by evaporating the filtrate (EtOH–hexane) to dryness] enabled the isolation of the *cis*-4,5-dihydrooxazole derivative (*cis*-**3a**, 5%). In addition, we succeeded in isolating the (*E*)-isomer from the reaction mixture obtained by the 0.5-h irradiation of (*Z*)-**1a** (conversion, 7%; Scheme 1). The structures of 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. Careful ^{1}H NMR spectral analysis of the product mixture suggested that there is very little formation of the *trans*-4,5-dihydrooxazole derivative (*trans*-**3a**) whose ring-proton signals with the $J_{4,5}$ value of 6.4 Hz were detected at 4.75 and 6.57 ppm,[7] though attempts to isolate *trans*-**3a** from the mixture were unsuccessful owing to its poor yield. The same product distribution was obtained by the irradiation of other α-dehydro(1-naphthyl)alaninamide derivatives (**1b–i**).

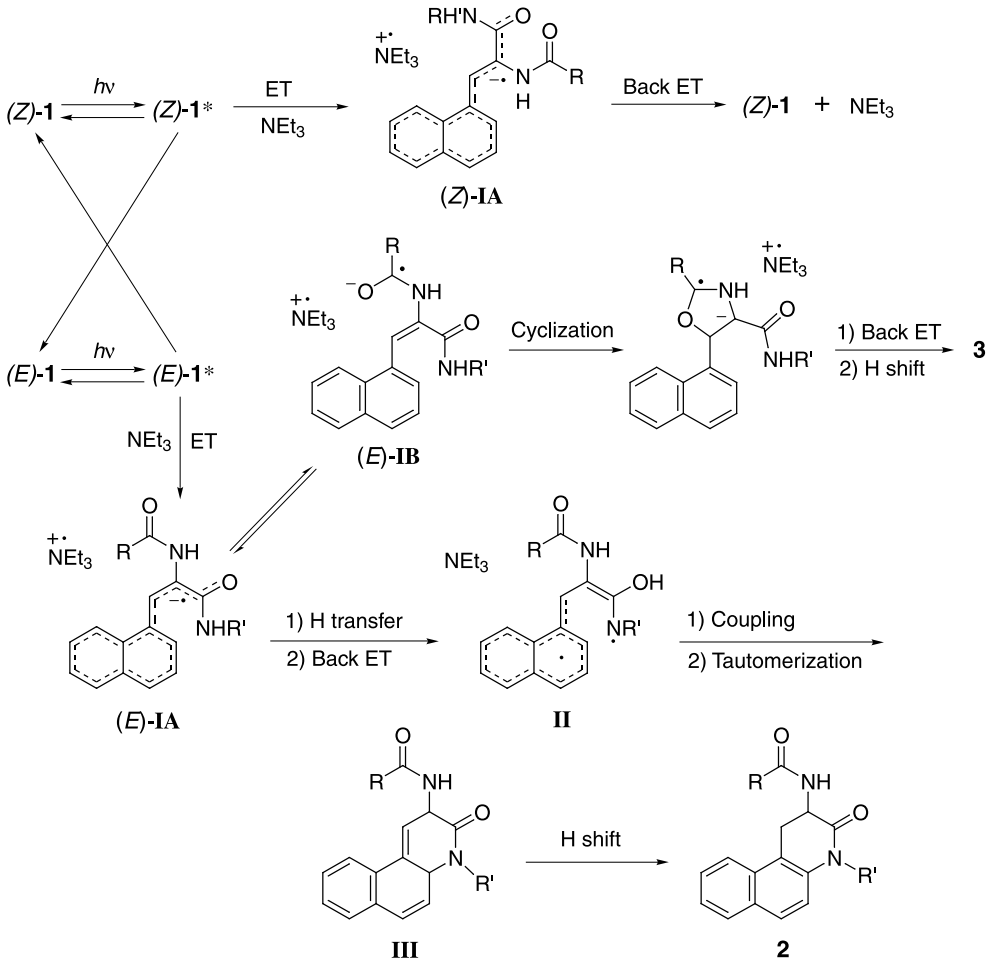
The finding that the photoproducts (**2a** and **3a**) are stable enough such that they undergo only negligible decomposition under the irradiation conditions employed (450 W high-pressure Hg lamp; Pyrex-filtered light; [(*Z*)-**1a**]=3.75×10^{-3} mol dm^{-3}; [TEA]=0.10 mol dm^{-3}) made it possible to monitor the reactions by means of ^{1}H NMR spectroscopy, as typically shown in Table 1. The result obtained for (*Z*)-**1a** demonstrates the rapid production of (*E*)-**1a** and the subsequent increase in compositions for **2a** and **3a** with the decrease of (*E*)- and (*Z*)-isomer compositions, being consistent with the mechanism in which the excited-state (*E*)- and (*Z*)-isomers serve as precursors of these products. Based on our previous findings,[6,7] we are able to propose Scheme 2 as the formation mechanism of dihydrobenzoquinolinone (**2**) and dihydrooxazole derivatives (**3**). The result that at the early stage of the reaction (0.5-h irradiation) the composition ratio of (*Z*)-**1a** to its isomer exhibits a negligible dependence on the TEA concentration (0–0.10 mol dm^{-3}) strongly suggests a minor contribution of the isomerization from (*Z*)-**1a**$^{-\cdot}$ to its isomer anion radical, (*E*)-**1a**$^{-\cdot}$. It is, thus, very likely that the (*Z*)-**1**-derived ion radical pair (*Z*)-**IA** undergoes an exclusive back ET to regenerate (*Z*)-**1** and TEA (Scheme 2). An ET from the ground-state TEA to the singlet excited-state (*E*)-isomer produces the ion radical pair intermediate (*E*)-**IA** which may be in equilibrium with the ion radical pair (*E*)-**IB** formed via intramolecular ET. Hydrogen transfer from the amide nitrogen to the amide carbonyl oxygen in the intermediate (*E*)-**IA** and the subsequent back ET to the TEA cation radical afford 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. In competition with this cyclization process, the nucleophilic attack of the *N*-acyl carbonyl oxygen anion upon the olefinic carbon in (*E*)-**IB** takes place to give the cyclized anion radical. A back ET to the TEA cation radical followed by



Scheme 1.

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

Irradiation time (h)	Composition (%)				
	(*Z*)-**1a**	(*E*)-**1a**	**2a**	*cis*-**3a**	*trans*-**3a**
0	100	0	0	0	0
0.5	85.6	12.8	1.4	0.2	0
3.0	52.8	25.3	19.7	1.9	0.3
5.0	36.1	20.5	39.3	3.5	0.6



Scheme 2.

hydrogen shift leads to *cis*- and *trans*-**3** (Scheme 2). Evidence in support of this mechanism comes from the finding that the free energy change (ΔG_{et}) for an ET from TEA to the singlet excited-state (*E*)-**1f** is -85 kJ mol^{-1}. This ΔG_{et} was estimated by using the simplified Weller equation: ΔG_{et}/kJ mol$^{-1}=96.5\ (E_{ox}-E_{red})-E_S$,[10] where E_{ox}, E_{red} and E_S refer to the oxidation potential of TEA (0.76 V vs. Ag/AgCl in MeCN), the reduction potential of (*E*)-**1f** (-2.09 V vs. Ag/AgCl in MeCN) and the first singlet excitation energy of (*E*)-**1f** (360 kJ mol^{-1} in MeCN), respectively. In addition, a methanol solution of **1a** (3.75×10^{-3} mol dm^{-3}) containing deuteriated TEA (0.10 mol dm^{-3}) was irradiated with Pyrex-filtered light from a 450 W high pressure Hg lamp for 3.0 h at room temperature. ^{1}H NMR spectral analysis of the product mixture in DMSO-d_6, obtained after usual work-up, clearly showed no disappearance of the 4.86 ppm signal which is ascribed to the proton attached to the 3-position of the dihydrobenzoquinolinone ring. This finding substantiates that proton transfer from the TEA cation radical to the (*E*)-**1**-derived anion radical occurs within the intermediate (*E*)-**IA** to, if any, only a small extent and, hence, consistent with the formation mechanism shown in Scheme 2.

In Table 2 is summarized composition of each compound obtained by the 0.5- and 5-h irradiation of methanol solutions of **1a–i** (3.75×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}) at room temperature (450 W high-pressure Hg lamp; Pyrex-filtered light). An inspection of Table 2 demonstrates that the reactivity of **1** has a clear propensity to decrease with increasing the electron-withdrawing ability of the substituent introduced at the *para*-position on the benzoyl benzene ring (**1b**>**1a**≈**1c**>**1d**≫**1e**). It is likely that anion radical produced by an ET from TEA migrates to the benzoyl moiety in the presence of stronger electron-withdrawing substituent to a more extent. Therefore, we see that the introduction of trifluoromethyl or cyano group promotes a back ET from the anion radical to the TEA cation radical to result in a decrease in the conversion of **1**. Additionally, the observation that the selectivity of **2** is also decreased by introducing these substituents allows us to propose that the shift of equilibrium between (*E*)-**IA** and (*E*)-**IB** to the latter intermediate lowers the relative rate for hydrogen abstraction in the former intermediate (Scheme 2). Taking into account the fact that the irradiation of **1b** having the electron-donating methoxy substituent at the *para*-position on the benzoyl benzene ring gives **2** in higher selectivity than that of **1a**, it can be predicted that the conversion of **1** and the selectivity of **2** is enhanced with decreasing the electron-withdrawing ability of aroyl group. From the data given in Table 2 we can see that the conversion of **1g** having the trimethylacetyl group is higher than that of **1a** having the benzoyl and also that the selectivity of **2g** is greater as compared to that of **2a**.

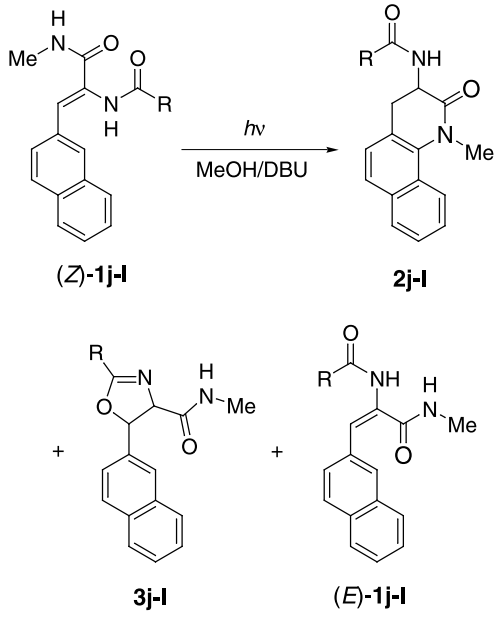
Table 2. Substituent effects on the conversion of **1** and selectivity of each compound, obtained by the irradiation of (*Z*)-**1** in MeOH containing TEA at room temperature

Compound	Irradiation time (h)	Composition (%)				Conversion[a] (%)	Selectivity of **2** (%)[b]
		(*Z*)-**1**	(*E*)-**1**	**2**	**3**[c]		
1a	0.5	85.6	12.8	1.4	0.2		
	5	36.1	20.5	39.3	4.1	43	91
1b	0.5	78.9	16.7	4.4	0		
	5	14.8	7.4	75.6	2.2	78	97
1c	0.5	87.0	11.6	1.3	0.2		
	5	40.0	21.8	34.2	3.9	38	90
1d	0.5	93.2	6.8	0	0		
	5	51.6	25.5	18.8	4.1	23	82
1e	0.5	97.9	2.1	0	0		
	10	60.1	25.0	11.1	3.8	15	74
1f	0.5	86.9	9.4	3.6	0		
	5	48.8	7.4	43.8	0	44	100
1g	0.5	79.3	18.2	2.5	0		
	5	21.6	16.9	59.9	1.6	62	97
1h	0.5	82.4	16.0	1.1	0.5		
	5	37.8	26.2	27.3	8.7	36	76
1i	0.5	82.7	16.0	0.6	0.4		
	5	36.4	28.2	28.6	6.7	35	81

[a] Conversion was estimated by the sum of compostion for **2** and **3**.
[b] Selectivity for **2** was evaluated by dividing the composition for **2** by the sum of compostion for **2** and **3**.
[c] The sum of composition for *cis*-**3** and *trans*-**3**.

Interestingly, ET-initiated photocyclization of **1f** bearing the 2,4-dimethoxybenzoyl group afforded **2f** in quantitative yield without forming **3f**, though the expected high conversion of **1f** was not attained. Because the rate for isomerization of (*Z*)-**1f** is much slower as compared to that of (*Z*)-**1b** (Table 2, 0.5-h irradiation), it is reasonable to explain the decreased photoreactivity of 2,4-dimethoxybenzoyl-substituted **1f** in terms of the enhanced deactivation of the excited-state (*Z*)-**1f**. Electronic effects of the *ortho*-methoxy group in the (*Z*)-isomer may play a role in slowing

Table 3. Composition of each compound, conversion of **1** and selectivity of **2**, obtained by the 5-h irradiation of (*Z*)-**1** in MeOH containing DBU at room temperature



Compound	Composition (%)				Conversion (%)	Selectivity of **2** (%)
	(*Z*)-**1**	(*E*)-**1**	**2**	**3**[a]		
1j	48.1	27.1	17.6	7.2	25	71
1k	53.8	15.2	25.7	5.3	31	83
1l	62.8	19.1	11.4	6.7	18	63

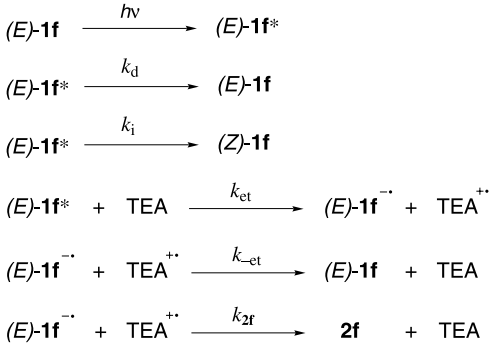
[a] The mixture of *cis*- and *trans*-isomers.

down the isomerization into (*E*)-**1f**. These considerations, therefore, substantiate the mechanism proposed by us.

In order to explore the scope and limitations of the observed ET-initiated photocyclization, we attempted PET reactions of α-dehydronaphthylalaninamides (**1j–l**) in which the 2-naphthyl group was introduced instead of the 1-naphthyl. When a methanol solution of **1j** (3.75×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}) was irradiated with Pyrex-filtered light from a 450 W high-pressure Hg lamp at room temperature, complicated product mixtures were obtained. However, the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.10 mol dm^{-3}) as an electron donor enabled the estimation of composition for each compound obtained by the 5-h irradiation of **1j**, as shown in Table 3. Because DBU possesses greater electron-donating ability than TEA, the presence of DBU is considered to markedly enhance the relative rate of ET process affording only the products derived from PET reaction. The same product distribution was observed by the irradiation of methanol solutions of **1k** and **1l** (Table 3). A comparison of the selectivity for **2a**,**b**,**f** with that for **2j–l** reveals that replacement of the 1-naphthyl group by the 2-naphthyl lowers the selectivity of a given dihydrobenzoquinolinone. The 2-naphthyl substituent in (*E*)-**1j–l** is considered to exert less steric hindrance than the 1-naphthyl in (*E*)-**1a–i** in the cyclization process from the anion radical in **IB**. This less steric hindrance accelerates the cyclization reaction that proceeds through **IB** to result in a decrease in the selectivity of **2** as observed.

2.2. Effects of TEA concentration on the quantum yield for formation of 2

As described in Section 2.1, the ET-initiated photocyclization of **1f** selectively produces the corresponding dihydrobenzoquinolinone derivative (**2f**). This result allows us to obtain quantitative information concerning the relative rates of ET and related processes (that control the formation efficiency of **2**), through analysis of the TEA concentration dependence of the quantum yield (Φ) for appearance of **2**. We are able to propose Scheme 3 based on the findings that the presence of TEA affects the rate for photoisomerization from (*E*)-**1** into (*Z*)-**1** to a negligible extent and, in addition, the singlet excited-state (*E*)-isomer serves as a precursor of **2**. In order to exclude the contribution of (*Z*)-**1f**-derived ET reaction process, quantum yields for the isomerization into (*Z*)-**1f** as well as for appearance of **2f** were determined at



Scheme 3.

less than 4% conversion of (*E*)-**1f** employed as the starting isomer. By applying the steady-state approximation to Scheme 3, we obtain Eqs. 1 and 2, where $\Phi_{\mathbf{2f}}$ and Φ_i refer to the quantum yields for the formation of **2f** and for the isomerization, respectively.

$$\Phi_{\mathbf{2f}}^{-1} = \left(1+\frac{k_{-et}}{k_{\mathbf{2f}}}\right)\left\{1+\frac{k_d+k_i}{k_{et}[TEA]}\right\} \quad (1)$$

$$\Phi_i = \frac{k_i}{(k_i+k_d)} \quad (2)$$

As typically depicted in Figure 1, there was a linear relationship between the reciprocals of $\Phi_{\mathbf{2f}}$ ($\Phi_{\mathbf{2f}}^{-1}$) and TEA concentration ([TEA]$^{-1}$). From the intercept and the ratio of slope to the intercept of linear plot obtained, we were able to evaluate the relative rates of ET and back ET processes, that is, the magnitude of $k_{et}/(k_d+k_i)$ and $k_{-et}/k_{\mathbf{2f}}$, respectively. Furthermore, there was no formation of **2f** when a methanol solution of (*E*)-**1f** containing no TEA was irradiated,[6] so that we were able to determine quantum yield for the isomerization (Φ_i) and then to estimate the relative rates of given processes by the use of Φ_i ($=0.35\pm0.01$) and Eqs. 3–5.

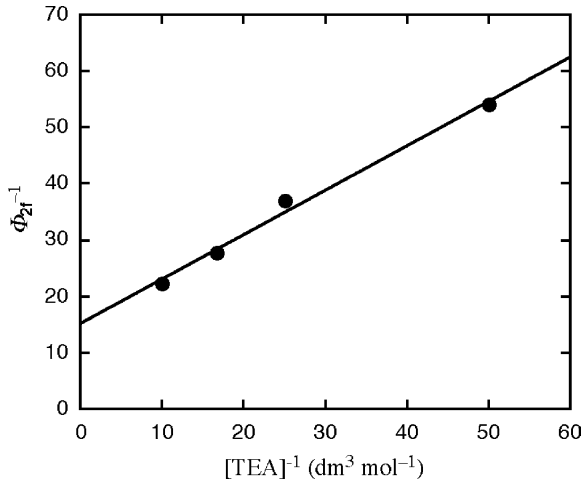


Figure 1. Double reciprocal plot of $\Phi_{\mathbf{2f}}^{-1}$ versus [TEA]$^{-1}$ for the ET-initiated photocyclization of (*E*)-**1f** in methanol at room temperature.

$$\frac{k_{et}}{\Phi_i(k_d+k_i)} = \frac{k_{et}}{k_i} \quad (3)$$

$$\Phi_i^{-1} - 1 = \frac{k_d}{k_i} \quad (4)$$

$$\left(\frac{k_{et}}{k_i}\right)\left(\frac{k_i}{k_d}\right) = \frac{k_{et}}{k_d} \quad (5)$$

In Table 4 are summarized these relative rates which demonstrate that the ET rate (k_{et}[TEA], [TEA]$=$ 0.10 mol dm^{-3}) is faster than the rate for deactivation and isomerization (k_d+k_i) of the excited-state (*E*)-**1f** by a factor of about 2. In addition, the magnitude of k_i/k_d confirms that isomerization into (*Z*)-**1f** is the minor deactivation pathway of the excited-state (*E*)-isomer in the absence of TEA. Despite the rapid progress of PET reaction, the $\Phi_{\mathbf{2f}}$ value

Table 4. Relative rates for given processes

k_i/k_d	$k_{et}[TEA]/k_d$[a]	$k_{et}[TEA]/k_i$[a]	$k_{et}[TEA]/(k_d+k_i)$[a]	k_{-et}/k_{2f}
0.54	2.9	5.4	1.9	14

[a] Value estimated at [TEA]=0.10 mol dm^{-3}.

was not so large (Φ_{2f}=0.045 at [TEA]=0.10 mol dm^{-3}). The fact that the rate for a back ET from the (*E*)-**1** anion radical to the TEA cation radical (k_{-et}) is 14 times as fast as that for the cyclization (k_{2f}), therefore, led us to conclude that the relative rate for this back ET is a major factor that controls the overall efficiency of PET reactions examined.

3. Conclusions

Although there are many synthetic methods for the construction of significant heterocyclic rings,[11] convenient photochemical route to dihydrobenzoquinolinone derivatives is scarcely known.[12] Because it is facile to prepare the starting *N*-aroyl-α-dehydronaphthylalaninamides (**1**) and related α-dehydroarylalaninamides, a wide variety of substituted dihydroquinolinones can be synthesized by the ET-initiated photocyclization of these alaninamide derivatives. The facts that dihydrobenzoquinolinones are extremely stable under irradiation conditions and then obtained in high selectivities render our PET reactions in methanol containing TEA or DBU very useful in constructing the dihydroquinolinone ring. We were also able to obtain quantitative information about the relative rates of ET and related processes, through analysis of the dependence of quantum yield for formation of **2** on the TEA concentration.

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. HPLC analysis was performed on a SHIMADZU LC-10AT high-performance liquid chromatography system equipped with a 4.6×250-mm ODS (Zorbax) column and a SHIMADZU SPD-10A UV detector (detection wavelength=240 nm; mobile phase, MeCN/H_2O=60:40, v/v). UV absorption and fluorescence spectra were measured at room temperature with a HITACHI U-3300 spectrophotometer and a HITACHI F-4500 spectrofluorimeter, respectively. A cell with a 10-mm pathlength was used. Elemental analysis was performed on a PERKIN–ELMER PE2400 series II CHNS/O analyzer. Oxidation and reduction potentials were measured with a YANACO P-1100 polarographic analyzer. Mass spectra were recorded on a JEOL JMS-01SG-2 spectrometer. MeOH was purified according to the standard procedure and freshly distilled prior to use. TEA and DBU were fractionally distilled from sodium hydroxide. All other reagents used were obtained from commercial sources and of the highest grade available.

A potassium tris(oxalato)ferrate(III) actinometer was employed to determine quantum yields for appearance of **2f** and (*Z*)-**1f** at low conversions of the starting (*E*)-**1f** (< 4%).[13] A 450 W high-pressure Hg lamp was used as the light source from which 313 nm light was selected with 1.0 wt% potassium carbonate solution of potassium chromate (2.0×10^{-3} mol dm^{-3}), CORNING 7-54 and TOSHIBA IRA-25S glass filters. Linear calibration curves for **2f** and (*Z*)-**1f**, made under the same analytical conditions, were utilized to quantify the formation of these two compounds. All of the quantum yields are an average of more than three determinations.

4.2. General procedure for the synthesis of (*Z*)-4-(1-naphthylmethylene)-2-(substituted phenyl)-5(4*H*)-oxazolones, (*Z*)-4-(2-naphthylmethylene)-2-(substituted phenyl)-5(4*H*)-oxazolones and (*Z*)-2-(*tert*-butyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone

N-(Substituted benzoyl)glycine or trimethylacetylglycine (0.04 mol), 1-naphthaldehyde or 2-naphthaldehyde (0.05 mol), and sodium acetate (0.02 mol) were added to acetic anhydride (25 mL) and the resulting mixture was heated at 65–75 °C for 1–2 h [*N*-(substituted benzoyl)glycine] or 6 h (*N*-trimethylacetylglycine) with stirring. The mixture was cooled with ice and the solid separated out was collected by filtration with suction and washed with water, a small amount 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 (50–70%).

4.2.1. (*Z*)-2-Phenyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 166.0–167.0 °C. IR (KBr): 1797, 1647, 1167 cm^{-1}. ^{1}H 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).

4.2.2. (*Z*)-2-(4-Methoxyphenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 207.0–208.0 °C. IR (KBr): 1788, 1644, 1170 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).

4.2.3. (*Z*)-2-(4-Bromophenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 201.0–201.5 °C. IR (KBr): 1799, 1650, 1180 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (1H, dd, *J*=7.6, 7.6 Hz), 7.63–7.66 (2H, m), 7.69 (2H, d, *J*=8.3 Hz), 7.92 (1H, d, *J*=8.2 Hz), 7.99 (1H, d, *J*=8.3 Hz), 8.07 (2H, d, *J*=8.3 Hz), 8.17 (1H, s), 8.31 (1H, d, *J*=8.2 Hz), 9.00 (1H, d, *J*=7.6 Hz).

4.2.4. (*Z*)-2-(4-Trifluoromethylphenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 201.0–202.0 °C. 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).

4.2.5. (*Z*)-2-(4-Cyanophenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 237.0–238.0 °C. 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).

4.2.6. (*Z*)-2-(2,4-Dimethoxyphenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 174.0–175.5 °C. IR (KBr): 1768, 1643, 1165 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.91 (3H, s), 4.01 (3H, s), 6.56 (1H, d, J=2.4 Hz), 6.63 (1H, dd, J=2.4, 8.5 Hz), 7.55 (1H, dd, J=7.3, 6.7 Hz), 7.6–7.60 (2H, m), 7.89 (1H, d, J=7.9 Hz), 7.94 (1H, d, J=8.5 Hz), 8.05 (1H, s), 8.08 (1H, d, J=8.5 Hz), 8.33 (1H, d, J=8.5 Hz), 9.07 (1H, d, J=7.3 Hz).

4.2.7. (*Z*)-2-(*tert*-Butyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 89.0–90.0 °C. IR (KBr): 1794, 1652, 1647, 1150 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.41 (9H, s), 7.54 (1H, dd, J=6.9, 8.2 Hz), 7.60 (1H, dd, J=7.6, 8.2 Hz), 7.61 (1H, dd, J=6.9, 8.9 Hz), 7.89 (1H, d, J=8.2 Hz), 7.94 (1H, d, J=8.2 Hz), 8.04 (1H, s), 8.27 (1H, d, J=8.9 Hz), 8.89 (1H, d, J=7.6 Hz).

4.2.8. (*Z*)-4-(2-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone. Mp 142.0–143.0 °C. IR (KBr): 1797, 1626, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.51 (1H, dd, J=7.9, 7.9 Hz), 7.54 (1H, dd, J=7.9, 7.9 Hz), 7.54 (2H, dd, J=7.9, 7.9 Hz), 7.61 (1H, dd, J=7.9, 7.9 Hz), 7.83 (1H, d, J=7.9 Hz), 7.89 (1H, d, J=8.5 Hz), 7.91 (1H, d, J=7.9 Hz), 8.19 (2H, d, J=7.9 Hz), 8.43 (1H, s), 8.49 (1H, d, J=8.5 Hz).

4.2.9. (*Z*)-2-(4-Methoxyphenyl)-4-(2-naphthylmethylene)-5(4*H*)-oxazolone. Mp 198.0–199.0 °C. IR (KBr): 1788, 1653, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.04 (2H, d, J=8.9 Hz), 7.32 (1H, s), 7.49–7.58 (2H, m), 7.83–7.94 (3H, m), 8.17 (2H, d, J=8.9 Hz), 8.46–8.52 (2H, m).

4.2.10. (*Z*)-2-(2,4-Dimethoxyphenyl)-4-(2-naphthylmethylene)-5(4*H*)-oxazolone. Mp 173.5–174.5 °C. IR (KBr): 1775, 1655, 1170 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.92 (3H, s), 4.06 (3H, s), 6.58 (1H, d, J=2.1 Hz), 6.64 (1H, dd, J=2.1, 8.6 Hz), 7.32 (1H, s), 7.51–7.56 (2H, m), 7.84–7.93 (3H, m), 8.08 (1H, d, J=8.6 Hz), 8.47 (1H, d, J=8.9 Hz), 8.56 (1H, s).

4.3. General procedure for the synthesis of (*Z*)-*N*-alkyl-3-(1-naphthyl)-2-(substituted benzoylamino)-2-propenamides [(*Z*)-1a–f,i], (*Z*)-*N*-methyl-3-(1-naphthyl)-2-trimethylacetylamino-2-propenamide [(*Z*)-1g], (*Z*)-3-(1-naphthyl)-2-benzoylamino-2-propenamide [(*Z*)-1h], and (*Z*)-*N*-methyl-3-(2-naphthyl)-2-(substituted benzoylamino)-2-propenamides [(*Z*)-1j–l]

(*Z*)-4-(1-Naphthylmethylene)-2-(substituted phenyl)-5(4*H*)-oxazolone (for **1a**–**f**,**h**,**i**, 0.010 mol), (*Z*)-2-(*tert*-butyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1g**, 0.010 mol) or (*Z*)-4-(2-naphthylmethylene)-2-(substituted phenyl)-5(4*H*)-oxazolone (for **1j**–**l**, 0.010 mol) was added to dry $CHCl_3$ (30 mL) containing primary amine (0.012 mol) and the resulting solution was stirred for 0.5–1 h at room temperature. After removal of the solvent under reduced pressure, the crystalline solid obtained was recrystallized twice from EtOH–hexane affording colorless crystals (50–80%).

4.3.1. (*Z*)-2-Benzoylamino-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1a]. Mp 205.0–206.0 °C. IR (KBr): 1650, 1670, 3080, 3300 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.75 (3H, d, J=4.9 Hz) 7.43 (2H, dd, J=7.3, 7.3 Hz), 7.43 (1H, dd, J=6.7, 7.9 Hz), 7.52 (1H, dd, J=7.3, 7.3 Hz), 7.54 (1H, dd, J=6.7, 7.0 Hz), 7.56 (1H, dd, J=6.7, 7.9 Hz), 7.62 (1H, d, J=6.7 Hz), 7.76 (1H, s), 7.84 (2H, d, J=7.3 Hz), 7.86 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=7.0 Hz), 8.04 (1H, d, J=7.9 Hz), 8.19 (1H, q, J=4.9 Hz), 9.75 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 124.2, 125.3, 125.99, 126.02, 126.03, 126.3, 127.8 (2C), 128.0 (2C), 128.4 (2C), 131.1, 131.5 (2C), 132.4, 133.1, 133.7, 165.2, 166.2. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (75.97); H, 5.49 (5.18); N, 8.48% (8.45%).

4.3.2. (*Z*)-2-(4-Anisoylamino)-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1b]. Mp 226.0–227.0 °C. IR (KBr): 1670, 1650, 3080, 3300 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.74 (3H, d, J=4.3 Hz), 3.79 (3H, s), 6.96 (2H, d, J=8.6 Hz), 7.42 (1H, dd, J=7.3, 7.9 Hz), 7.57–7.53 (2H, m), 7.60 (1H, d, J=7.3 Hz), 7.71 (1H, s), 7.83 (2H, d, J=8.6 Hz), 7.85 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=7.6 Hz), 8.03 (1H, d, J=7.9 Hz), 8.16 (1H, q, J=4.3 Hz), 9.61 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 55.4, 113.3 (2C), 124.3, 125.4, 125.5, 126.0 (2C), 126.03, 126.4, 128.38, 128.40, 129.8 (2C), 131.2 (2C), 131.5, 132.6, 161.9, 165.4, 165.7. Anal. Calcd (found) for $C_{22}H_{20}N_2O_3$: C, 73.32 (73.53); H, 5.59 (5.51); N, 7.77% (7.37%).

4.3.3. (*Z*)-2-(4-Bromobenzoylamino)-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1c]. Mp 220.0–221.0 °C. IR (KBr): 1630, 1650, 3200, 3350 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.74 (3H, d, J=4.9 Hz), 7.43 (1H, dd, J=7.3, 7.9 Hz), 7.56–7.52 (2H, m), 7.58 (1H, d, J=7.3 Hz), 7.66 (2H, d, J=8.6 Hz), 7.76 (1H, s), 7.78 (2H, d, J=8.6 Hz), 7.86 (1H, d, J=7.9 Hz), 7.93 (1H, d, J=9.2 Hz), 8.02 (1H, d, J=7.3 Hz), 8.22 (1H, q, J=4.9 Hz), 9.84 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 124.2, 125.3, 125.4, 125.99, 126.00, 126.3, 126.4, 128.4, 128.5, 130.0 (2C), 131.1, 131.13 (2C), 131.4, 132.1, 132.9, 133.1, 165.0, 165.3. Anal. Calcd (found) for $C_{21}H_{17}Br_1N_2O_2$: C, 61.63 (61.26); H, 4.19 (3.90); N, 6.84% (7.00%).

4.3.4. (*Z*)-*N*-Methyl-3-(1-naphthyl)-2-(4-trifluoromethylbenzoylamino)-2-propenamide [(*Z*)-1d]. Mp 195.0–196.0 °C. IR (KBr): 1650, 1675, 3170, 3290 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.76 (3H, d, J=4.9 Hz), 7.44 (1H, dd, J=6.7, 7.9 Hz), 7.54 (1H, dd, J=6.1, 7.3 Hz), 7.57 (1H, dd, J=6.1, 8.9 Hz), 7.61 (1H, d, J=6.7 Hz), 7.81 (1H, s), 7.83 (2H, d, J=7.9 Hz), 7.87 (1H, d, J=7.9 Hz),

7.94 (1H, d, J=8.9 Hz), 8.03 (2H, d, J=7.9 Hz), 8.03 (1H, d, J=7.3 Hz), 8.26 (1H, q, J=4.9 Hz), 10.01 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 123.9 (1C, q, J=273.1 Hz), 124.2, 125.1 (2C, q, J=3.0 Hz), 125.4, 126.0, 126.1, 126.4, 126.7, 128.5, 128.6, 128.7 (2C), 131.1, 131.3, 131.5 (1C, q, J=31.0 Hz), 131.9, 133.2, 137.6, 164.9, 165.1. Anal. Calcd (found) for $C_{22}H_{17}F_3N_2O_2$: C, 66.33 (66.12); H, 4.30 (4.06); N, 7.03% (7.16%).

4.3.5. (*Z*)-2-(4-Cyanobenzoylamino)-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1e]. Mp 210.0–211.0 °C. IR (KBr): 1650, 1670, 2230, 3290, 3400 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.74 (3H, d, J=4.9 Hz), 7.42 (1H, dd, J=7.3, 8.5 Hz), 7.52–7.55 (2H, m), 7.57 (1H, d, J=7.3 Hz), 7.79 (1H, s), 7.85 (1H, d, J=8.5 Hz), 7.96–7.91 (5H, m), 8.00 (1H, d, J=7.3 Hz), 8.24 (1H, q, J=4.9 Hz), 9.99 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 113.8, 118.3, 124.2, 125.4, 126.0, 126.1, 126.4, 126.8, 128.5 (2C), 128.6 (2C), 131.1, 131.3, 131.8, 132.2 (2C), 133.2, 137.8, 164.8, 164.9. Anal. Calcd (found) for $C_{22}H_{17}N_3O_2$: C, 74.35 (73.98); H, 4.82 (4.72); N, 11.82% (12.14%).

4.3.6. (*Z*)-2-(2,4-Dimethoxybenzoylamino)-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1f]. Mp 176.0–176.5 °C. IR (KBr): 1640, 1665, 3348 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.76 (3H, d, J=4.3 Hz), 3.59 (3H, s), 3.79 (3H, s), 6.58 (1H, d, J=2.5 Hz), 6.62 (1H, dd, J=2.5, 8.9 Hz), 7.27 (1H, s), 7.54–7.57 (3H, m), 7.62 (1H, d, J=7.3 Hz), 7.77 (1H, d, J=8.9 Hz), 7.92 (1H, d, J=7.9 Hz), 7.98–7.96 (1H, m), 8.08–8.06 (1H, m), 8.22 (1H, q, J=4.3 Hz), 9.47 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.2, 55.6, 56.0, 98.5, 106.1, 113.6, 120.1, 124.5, 125.4, 126.10, 126.15, 126.4, 128.2, 128.4, 130.9, 131.4, 132.7, 133.2, 133.4, 158.6, 162.6, 163.4, 165.4. Anal. Calcd (found) for $C_{23}H_{22}N_2O_4$: C, 70.75 (70.41); H, 5.68 (5.61); N, 7.17% (6.87%).

4.3.7. (*Z*)-*N*-Methyl-3-(1-naphthyl)-2-trimethylacetylamino-2-propenamide [(*Z*)-1g]. Mp 180.0–181.5 °C. IR (KBr): 1630, 1650, 3300, 3350 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.03 (9H, s), 2.75 (3H, d, J=4.9 Hz), 7.47 (1H, dd, J=7.3, 7.9 Hz), 7.53–7.55 (4H, m), 7.84 (1H, q, J=4.9 Hz), 7.88 (1H, d, J=7.9 Hz), 7.93–7.95 (1H, m), 7.98–8.00 (1H, m), 8.75 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 26.9 (3C), 38.3, 124.4, 124.8, 125.2, 125.9, 126.2, 126.3, 128.3, 128.4, 131.0, 131.5, 132.8, 133.1, 165.6, 176.9. Anal. Calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.80); H, 7.14 (7.04); N, 9.03% (9.10%).

4.3.8. (*Z*)-2-Benzoylamino-3-(1-naphthyl)-2-propenamide [(*Z*)-1h]. Mp 159.5–160.0 °C. IR (KBr): 1650, 1690, 3190, 3280 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.30 (1H, br s), 7.41 (2H, dd, J=7.3, 7.3 Hz), 7.43 (1H, dd, J=7.3, 8.5 Hz), 7.50 (1H, dd, J=7.3, 7.3 Hz), 7.54 (1H, dd, J=6.7, 8.6 Hz), 7.57 (1H, dd, J=6.7, 7.9 Hz), 7.62 (1H, d, J=7.3 Hz), 7.75 (1H, s), 7.75 (1H, br s), 7.82 (2H, d, J=7.3 Hz), 7.85 (1H, d, J=8.5 Hz), 7.92 (1H, d, J=8.6 Hz), 8.04 (1H, d, J=7.9 Hz), 9.71 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 124.3, 125.4, 126.1, 126.2 (2C), 126.4, 127.8 (2C), 128.2 (2C), 128.47, 128.5, 131.2, 131.5, 131.6, 132.5, 133.2, 133.9, 166.2, 166.7. Anal. Calcd (found) for $C_{20}H_{16}N_2O_2$: C, 75.93 (75.61); H, 5.10 (5.13); N, 8.86% (8.96%).

4.3.9. (*Z*)-2-Benzoylamino-*N*-benzyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1i]. Mp 178.0–178.5 °C. IR (KBr): 1610, 1650, 3060, 3250 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.47 (2H, d, J=6.1 Hz), 7.25 (1H, dd, J=7.3, 7.3 Hz), 7.34 (2H, dd, J=7.3, 7.3 Hz), 7.40 (2H, d, J=7.3 Hz), 7.42–7.46 (3H, m), 7.52 (1H, dd, J=7.9, 7.9 Hz), 7.55 (1H, dd, J=7.3, 8.5 Hz), 7.58 (1H, dd, J=7.3, 7.9 Hz), 7.66 (1H, d, J=6.7 Hz), 7.84 (1H, s), 7.86 (2H, d, J=7.9 Hz), 7.86 (1H, d, J=7.9 Hz), 7.94 (1H, d, J=8.5 Hz), 8.05 (1H, d, J=7.9 Hz), 8.84 (1H, t, J=6.1 Hz), 9.83 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 42.6, 124.3, 125.4, 126.0, 126.1, 126.4, 126.6 (2C), 127.2 (2C), 127.9 (2C), 128.1, 128.2, 128.45, 128.53, 131.1, 131.4, 131.5 (2C), 132.4, 133.2 (2C), 133.8, 139.8, 164.9, 166.4. Anal. Calcd (found) for $C_{27}H_{22}N_2O_2$: C, 79.78 (79.51); H, 5.46 (5.87); N, 6.89% (6.70%).

4.3.10. (*Z*)-2-Benzoylamino-*N*-methyl-3-(2-naphthyl)-2-propenamide [(*Z*)-1j]. Mp 189.0–190.0 °C. IR (KBr): 1628, 3052, 3248 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.72 (3H, d, J=4.9 Hz) 7.42 (1H, s), 7.49 (1H, dd, J=6.7, 7.6 Hz), 7.50 (1H, dd, J=6.7, 7.6 Hz), 7.53 (2H, dd, J=7.3, 7.9 Hz), 7.60 (1H, dd, J=7.9, 7.9 Hz), 7.71 (1H, d, J=8.5 Hz), 7.78 (1H, d, J=6.7 Hz), 7.83 (1H, d, J=8.5 Hz), 7.85 (1H, d, J=6.7 Hz), 8.03 (2H, d, J=7.9 Hz), 8.08 (1H, s), 8.14 (1H, q, J=4.9 Hz), 9.98 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 126.1, 126.5, 126.7, 127.4, 127.7, 127.9 (2C), 128.0, 128.3 (2C), 128.8, 129.3, 130.5, 131.6, 132.0, 132.6, 132.7, 133.8, 165.4, 165.9. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.30); H, 5.49 (5.60); N, 8.48% (8.31%).

4.3.11. (*Z*)-2-(4-Anisoylamino)-*N*-methyl-3-(2-naphthyl)-2-propenamide [(*Z*)-1k]. Mp 138.0–139.5 °C. IR (KBr): 1610, 1640, 3090, 3250 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.72 (3H, d, J=4.6 Hz), 3.84 (3H, s), 7.07 (2H, d, J=8.9 Hz), 7.38 (1H, s), 7.48–7.52 (2H, m), 7.70 (1H, d, J=8.5 Hz), 7.78 (1H, d, J=8.5 Hz), 7.82 (1H, d, J=8.5 Hz), 7.85 (1H, d, J=7.2 Hz), 8.02 (2H, d, J=8.9 Hz), 8.06 (1H, s), 8.13 (1H, q, J=4.6 Hz), 9.85 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3, 55.4, 113.5 (2C), 126.1, 126.2, 126.5, 126.7, 127.4, 127.7, 128.0, 128.5, 129.3, 129.9 (2C), 130.7, 132.1, 132.6, 132.8, 162.0, 165.5, 165.6. Anal. Calcd (found) for $C_{22}H_{20}N_2O_3$: C, 73.32 (72.98); H, 5.59 (5.93); N, 7.77% (7.43%).

4.3.12. (*Z*)-2-(2,4-Dimethoxybenzoylamino)-*N*-methyl-3-(2-naphthyl)-2-propenamide [(*Z*)-1l]. Mp 173.5–174.5 °C. IR (KBr): 1630, 1643, 3323 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.72 (3H, d, J=4.6 Hz), 3.85 (3H, s), 3.89 (3H, s), 6.68 (1H, dd, J=2.3, 8.6 Hz), 6.74 (1H, dd, J=2.3 Hz), 7.12 (1H, s), 7.51–7.53 (2H, m), 7.74 (1H, d, J=8.6 Hz), 7.82–7.90 (4H, m), 8.06 (1H, q, J=4.6 Hz), 8.10 (1H, s), 9.63 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.2, 55.6, 56.2, 98.5, 106.0, 114.3, 125.3, 126.3, 126.5, 126.6, 127.5, 127.8, 128.0, 128.8, 130.8, 132.1, 132.5, 132.7, 132.8, 158.9, 163.4 (2C), 165.6. Anal. Calcd (found) for $C_{23}H_{22}N_2O_4$: C, 70.75 (70.93); H, 5.68 (6.01); N, 7.17% (7.08%).

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

In order to examine the dependence of product distribution

and composition on irradiation time, a MeOH solution (45 mL) of (*Z*)-**1** (3.75×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}, for **1a–i**), or DBU (0.10 mol dm^{-3}, for **1j–l**) placed in a Pyrex vessel, was irradiated under nitrogen at room temperature with Pyrex-filtered light from a 450 W high-pressure Hg lamp (external irradiation). 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 ^{1}H NMR spectral analysis. When DBU was used as an electron donor, the resulting residue was at first dissolved in $CHCl_3$ and subsequently washed with 0.2 mol dm^{-3} HCl solution (20 mL). After removal of $CHCl_3$ under reduced pressure, the resulting residue was dissolved in DMSO-d_6 and subjected to ^{1}H NMR spectral analysis. The product composition was estimated from the area ratio of a given ^{1}H NMR signal for each compound.

On the other hand, a MeOH solution (200 mL) of (*Z*)-**1a–l** (3.75×10^{-3} mol dm^{-3}) containing TEA (0.10 mol dm^{-3}, for **1a–i**) or DBU (0.10 mol dm^{-3}, for **1j–l**), 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 (internal irradiation). After 3-h (**1b**), 6-h (**1a**,**c**,**f–l**), 10-h (**1d**), or 30-h (**1e**) 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 spectral analysis in DMSO-d_6. DBU was removed according to the same procedure as above. The remaining solutions of **1a–l** were concentrated to dryness under reduced pressure. The resulting residues were washed with a small amount of EtOH, allowing us to obtain analytical-grade **2a–l**. The combined filtrates were concentrated to dryness and subjected to column chromatography over silica gel (230 mesh, Merck) eluting with EtOAc–hexane. 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**,**f**,**h–j**], 3,4-dihydrobenzo[*f*]quinolinones (**2a–i**), 3,4-dihydrobenzo[*h*]quinolinones (**2j–l**) and 4,5-dihydrooxazoles (*cis*-**3a**,**h**,**i**) are as follows. Conversion was estimated by the sum of composition for **2** and **3**.

4.4.1. (*E*)-1a. Yield, 10% (conversion, 7%). Mp 171.0–172.0 °C. IR (KBr): 1678, 1664, 3264, 3320 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.46 (3H, d, J=4.9 Hz), 7.33 (1H, s), 7.43–7.47 (2H, m), 7.54 (2H, dd, J=7.3, 7.9 Hz), 7.54–7.58 (2H, m), 7.61 (1H, dd, J=7.3, 7.3 Hz), 7.83 (1H, d, J=7.3 Hz), 7.83 (1H, q, J=4.9 Hz), 7.94 (1H, d, J=6.4 Hz), 7.98 (2H, d, J=7.9 Hz), 8.07 (1H, d, J=7.9 Hz), 10.27 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.7, 115.7, 124.4, 125.3, 125.4, 125.8, 126.0, 127.3, 127.7 (2C), 128.2, 128.3 (2C), 131.2, 131.7, 132.0, 133.0, 133.7, 134.8, 164.8, 164.9. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.34); H, 5.49 (5.81); N, 8.48% (8.47%).

4.4.2. (*E*)-1f. Yield, 6% (conversion, 12%). Mp 191.0–192.0 °C. IR (KBr): 1608, 1636, 2945, 3347 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.45 (3H, d, J=4.8 Hz), 3.87 (3H, s), 4.00 (3H, s), 6.72 (1H, dd, J=2.1, 8.6 Hz), 6.74 (1H, d, J=2.1 Hz), 7.38 (1H, d, J=7.6 Hz), 7.46 (1H, dd, J=7.6, 7.9 Hz), 7.54–7.60 (2H, m), 7.65 (1H, q, J=4.8 Hz), 7.84 (1H, d, J=8.6 Hz), 7.92–7.95 (2H, m), 7.93 (1H, s), 8.08 (1H, d, J=7.9 Hz), 9.96 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.9, 55.6, 56.4, 98.7, 106.3, 114.0, 114.1, 124.6, 125.4, 125.7, 125.9, 126.1, 127.4, 128.3, 131.3, 132.4, 132.7, 133.2, 133.8, 158.7, 162.8, 163.5, 165.3. Anal. Calcd (found) for $C_{23}H_{22}N_2O_4$: C, 70.75 (70.62); H, 5.68 (5.77); N, 7.17% (7.32%).

4.4.3. (*E*)-1h. Yield, 12% (conversion, 6%). Mp 160.5–161.5 °C. IR (KBr): 1666, 1690, 3368, 3464 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.14 (1H, br s), 7.30 (1H, s), 7.34 (1H, br s), 7.46 (1H, dd, J=7.3, 8.2 Hz), 7.54 (2H, dd, J=7.3, 8.5 Hz), 7.54–7.58 (3H, m), 7.61 (1H, dd, J=7.3, 7.3 Hz), 7.84 (1H, d, J=8.2 Hz), 7.93–7.95 (1H, m), 7.99 (2H, d, J=8.5 Hz), 8.05–8.07 (1H, m), 10.24 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 116.2, 124.6, 125.4, 125.9, 126.0, 126.1, 127.4, 127.7 (2C), 128.26 (2C), 128.32 (2C), 131.3, 131.7, 132.3, 133.1, 133.9, 165.0, 166.0. Anal. Calcd (found) for $C_{20}H_{16}N_2O_2$: C, 75.93 (75.72); H, 5.10 (5.35); N, 8.86% (8.75%).

4.4.4. (*E*)-1i. Yield, 10% (conversion, 6%). Mp 155.5–157.0 °C. IR (KBr): 1627, 1644, 3256, 3330 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.19 (2H, d, J=6.1 Hz), 6.97–6.99 (2H, m), 7.14–7.16 (3H, m), 7.32 (1H, s), 7.33 (1H, dd, J=7.3, 8.5 Hz), 7.42 (1H, d, J=6.7 Hz), 7.53–7.57 (2H, m), 7.55 (2H, dd, J=7.3, 7.9 Hz), 7.62 (1H, dd, J=7.9, 7.9 Hz), 7.84 (1H, d, J=8.5 Hz), 7.94 (1H, d, J=7.9 Hz), 8.01 (2H, d, J=7.3 Hz), 8.07 (2H, d, J=7.3 Hz), 8.44 (1H, t, J=6.1 Hz), 10.34 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 42.3, 124.7, 125.4, 125.9, 126.0 (2C), 126.4, 127.3 (2C), 127.4 (2C), 127.8 (2C), 127.9 (2C), 128.3, 128.4 (2C), 131.4, 131.8, 132.1, 133.1, 133.9, 134.9, 138.9, 164.6, 165.0. Anal. Calcd (found) for $C_{27}H_{22}N_2O_2$: C, 79.78 (79.37); H, 5.46 (5.87); N, 6.89% (6.80%).

4.4.5. (*E*)-1j. Yield, 10% (conversion, 4%). Mp 167.0–168.0 °C. IR (KBr): 1643, 3059, 3260 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.60 (3H, d, J=4.9 Hz), 6.89 (1H, s), 7.43 (1H, d, J=8.5 Hz), 7.47 (1H, dd, J=7.3, 7.3 Hz), 7.49 (1H, dd, J=7.3, 7.3 Hz), 7.53 (2H, dd, J=7.3, 8.3 Hz), 7.60 (1H, dd, J=7.3, 7.3 Hz), 7.79 (1H, s), 7.83 (1H, d, J=7.3 Hz), 7.85 (1H, d, J=8.5 Hz), 7.95 (2H, d, J=8.3 Hz), 8.08 (1H, q, J=4.9 Hz), 10.20 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.8, 118.0, 125.9, 126.1, 126.2, 126.9, 127.3 (2C), 127.7 (3C), 128.3 (2C), 131.7, 131.9, 132.7, 132.9, 133.8, 133.9, 164.8, 165.1. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.18); H, 5.49 (5.32); N, 8.48% (8.40%).

4.4.6. 3-Benzoylamino-3,4-dihydro-1-methyl-2(1*H*)-benzo[*f*]quinolinone (2a). Yield, 67% (conversion, >99%). Mp 167.0–168.0 °C. IR (KBr): 1630, 1690, 3090, 3340 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.28 (1H, dd, J=15.3, 15.3 Hz), 3.45 (3H, s), 3.74 (1H, dd, J=6.7, 15.3 Hz), 4.86 (1H, ddd, J=6.7, 8.5, 15.3 Hz), 7.46 (1H, dd, J=6.7, 7.3 Hz), 7.52 (1H, d, J=8.5 Hz), 7.53 (2H, dd, J=6.7, 7.3 Hz), 7.57 (1H, dd, J=6.7, 8.5 Hz), 7.59 (1H, dd, J=7.3, 7.3 Hz), 7.93 (1H, d, J=7.3 Hz), 7.96 (2H, d, J=6.7 Hz), 7.96 (1H, d, J=8.5 Hz), 8.06 (1H, d, J=8.5 Hz), 8.86 (1H, d, J=8.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.7, 30.4, 48.5, 116.1, 117.6, 123.0, 124.5, 127.1, 127.3 (2C), 128.1, 128.4 (3C), 129.6, 130.5, 131.5, 134.1, 137.2, 166.2,

168.3. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.10); H, 5.49 (5.50); N, 8.48% (8.70%).

4.4.7. 3-(4-Anisoylamino)-3,4-dihydro-1-methyl-2(1*H*)-benzo[*f*]quinolinone (2b). Yield, 80% (conversion, >99%). Mp 172.0–173.0 °C. IR (KBr): 1640, 1690, 3300, 3400 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.25 (1H, dd, J=14.7, 15.3 Hz), 3.33 (3H, s), 3.44 (3H, s), 3.72 (1H, dd, J=6.1, 15.3 Hz), 4.84 (1H, ddd, J=6.1, 7.9, 14.7 Hz), 7.06 (2H, d, J=9.2 Hz), 7.45 (1H, dd, J=7.3, 7.9 Hz), 7.51 (1H, d, J=9.2 Hz), 7.56 (1H, dd, J=7.9, 8.5 Hz), 7.96–7.92 (4H, m), 8.06 (1H, d, J=8.5 Hz), 8.70 (1H, d, J=7.9 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.7, 30.3, 48.3, 55.3, 113.5 (2C), 116.0, 117.6, 123.0, 124.4, 126.2, 126.9, 127.9, 128.3, 129.1 (2C), 129.5, 130.5, 137.1, 161.6, 165.5, 168.4. Anal. Calcd (found) for $C_{22}H_{20}N_2O_3$: C, 73.32 (73.69); H, 5.59 (5.63); N, 7.77% (7.78%).

4.4.8. 3-(4-Bromobenzoylamino)-3,4-dihydro-1-methyl-2(1*H*)-benzo[*f*]quinolinone (2c). Yield, 77% (conversion, >99%). Mp 209.0–210.0 °C. IR (KBr): 1640, 1685, 3300, 3350 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.26 (1H, dd, J=14.7, 15.3 Hz) 3.44 (3H, s), 3.73 (1H, dd, J=6.1, 15.3 Hz), 4.84 (1H, ddd, J=6.1, 8.5, 14.7 Hz), 7.46 (1H, dd, J=6.7, 7.9 Hz), 7.51 (1H, d, J=9.2 Hz), 7.56 (1H, dd, J=7.3, 7.9 Hz), 7.75 (2H, d, J=8.5 Hz), 7.91 (2H, d, J=8.5 Hz), 7.93 (1H, d, J=9.2 Hz), 7.95 (1H, d, J=6.7 Hz), 8.06 (1H, d, J=7.3 Hz), 8.98 (1H, d, J=8.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.6, 30.4, 48.6, 116.1, 117.5, 123.1, 124.6, 125.3, 127.1, 128.1, 128.4, 129.6 (2C), 129.7, 130.6, 131.5 (2C), 133.2, 137.2, 165.4, 168.2. Anal. Calcd (found) for $C_{21}H_{17}BrN_2O_2$: C, 61.63 (61.47); H, 4.19 (4.20); N, 6.84% (7.08%).

4.4.9. 3,4-Dihydro-1-methyl-3-(4-trifluoromethylbenzoylamino)-2(1*H*)-benzo[*f*]quinolinone (2d). Yield, 75% (conversion, >99%). Mp 213.0–214.0 °C. IR (KBr): 1640, 1690, 3310 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.28 (1H, dd, J=14.6, 15.3 Hz), 3.45 (3H, s), 3.77 (1H, dd, J=6.1, 15.3 Hz), 4.88 (1H, ddd, J=6.1, 8.5, 14.6 Hz), 7.46 (1H, dd, J=7.3, 7.9 Hz), 7.52 (1H, d, J=8.6 Hz), 7.56 (1H, dd, J=7.3, 8.5 Hz), 7.93 (2H, d, J=8.2 Hz), 7.94 (1H, d, J=7.9 Hz), 7.96 (1H, d, J=8.6 Hz), 8.07 (1H, d, J=8.5 Hz), 8.16 (2H, d, J=8.2 Hz), 9.15 (1H, d, J=8.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.5, 30.4, 48.6, 116.1, 117.5, 123.1, 123.9 (1C, q, J=272.1 Hz), 124.5, 125.4 (2C, q, J=4.1 Hz), 127.0, 128.1, 128.3 (2C), 128.34, 129.6, 130.5, 131.3 (1C, q, J=31.0 Hz), 137.1, 137.9, 165.1, 168.1. Anal. Calcd (found) for $C_{22}H_{17}F_3N_2O_2$: C, 66.20 (66.20); H, 4.30 (3.97); N, 7.03% (6.87%).

4.4.10. 3-(4-Cyanobenzoylamino)-3,4-dihydro-1-methyl-2(1*H*)-benzo[*f*]quinolinone (2e). Yield, 60% (conversion, >99%). Mp 217.0–218.0 °C. IR (KBr): 1632, 1674, 2230, 3316 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.27 (1H, dd, J=15.2, 15.2 Hz), 3.44 (3H, s), 3.76 (1H, dd, J=6.7, 15.2 Hz), 4.86 (1H, ddd, J=6.7, 8.5, 15.2 Hz), 7.46 (1H, dd, J=6.7, 7.3 Hz), 7.52 (1H, d, J=8.6 Hz), 7.57 (1H, dd, J=6.7, 8.5 Hz), 7.93 (1H, d, J=7.3 Hz), 7.95 (1H, d, J=8.6 Hz), 8.03 (2H, d, J=8.6 Hz), 8.06 (1H, d, J=8.5 Hz), 8.11 (2H, d, J=8.6 Hz), 9.17 (1H, d, J=8.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.4, 30.3, 48.6, 113.7, 116.0, 117.4, 118.2, 123.0, 124.5, 127.0, 128.0, 128.1 (2C), 128.3, 129.6, 130.4, 132.4 (2C), 137.0, 138.0, 164.8, 167.9. Anal. Calcd (found) for $C_{22}H_{17}N_3O_2$: C, 74.35 (74.36); H, 4.82 (4.86); N, 11.82% (11.71%).

4.4.11. 3,4-Dihydro-3-(2,4-dimethoxybenzoylamino)-1-methyl-2(1*H*)-benzo[*f*]quinolinone (2f). Yield, 87% (conversion, >99%). Mp 198.0–199.0 °C. IR (KBr): 1610, 1643, 3352 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.05 (1H, dd, J=15.3, 14.7 Hz), 3.47 (3H, s), 3.86 (3H, s), 3.99 (3H, s), 4.04 (1H, dd, J=15.3, 6.1 Hz), 4.63 (1H, ddd, J=14.7, 6.1, 5.5 Hz), 6.69 (1H, dd, J=8.8, 2.4 Hz), 6.73 (1H, d, J=2.4 Hz), 7.47 (1H, d, J=7.3, 6.7 Hz), 7.53 (1H, d, J=9.2 Hz), 7.58 (1H, dd, J=8.5, 6.7 Hz), 7.94 (1H, d, J=9.2 Hz), 7.95 (1H, d, J=7.3 Hz), 7.98 (1H, d, J=8.8 Hz), 8.03 (1H, d, J=8.5 Hz), 8.90 (1H, d, J=5.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.4, 164.0, 163.3, 159.0, 137.0, 132.8, 130.6, 129.7, 128.4, 128.0, 127.1, 124.6, 123.1, 118.0, 116.2, 113.7, 106.0, 98.7, 56.3, 55.5, 49.2, 30.5, 26.6. Anal. Calcd (found) for $C_{22}H_{22}N_2O_4$: C, 70.75 (70.43); H, 5.68 (5.41); N, 7.17% (7.13%).

4.4.12. 3,4-Dihydro-1-methyl-3-trimethylacetylamino-2(1*H*)-benzo[*f*]quinolinone (2g). Yield, 75% (conversion, >99%). Mp 220.0–221.5 °C. IR (KBr): 1650, 1690, 3360 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.20 (9H, s), 3.15 (1H, dd, J=14.6, 15.3 Hz), 3.41 (3H, s), 3.60 (1H, dd, J=6.7, 15.3 Hz), 4.59 (1H, ddd, J=6.7, 7.3, 14.6 Hz), 7.44 (1H, dd, J=7.3, 7.3 Hz), 7.48 (1H, d, J=8.6 Hz), 7.56 (1H, dd, J=7.3, 8.5 Hz), 7.76 (1H, d, J=7.3 Hz), 7.92 (1H, d, J=7.3 Hz), 7.93 (1H, d, J=8.6 Hz), 8.02 (1H, d, J=8.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.5, 27.4 (3C), 30.3, 38.2, 47.9, 116.1, 117.7, 123.0, 124.5, 127.0, 127.9, 128.3, 129.6, 130.5, 137.1, 168.5, 177.5. Anal. Calcd (found) for $C_{19}H_{22}N_2O_2$: C, 73.52 (73.92); H, 7.14 (7.21); N, 9.03% (9.18%).

4.4.13. 3-Benzoylamino-3,4-dihydro-2(1*H*)-benzo[*f*]quinolinone (2h). Yield, 59% (conversion, 94%). Mp 184.0–186.0 °C. IR (KBr): 1650, 1680, 1746, 2944, 3404 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.54 (3H, d, J=6.7 Hz), 3.29 (1H, dd, J=15.2, 14.6 Hz), 3.62 (3H, s), 3.70 (1H, dd, J=15.2, 6.1 Hz), 4.80 (1H, ddd, J=14.6, 8.6, 6.1 Hz), 5.35 (1H, q, J=6.7 Hz), 7.48 (1H, dd, J=7.9, 7.9 Hz), 7.52 (2H, dd, J=7.3, 7.9 Hz), 7.58 (1H, d, J=9.2 Hz), 7.58–7.60 (2H, m), 7.94 (1H, d, J=9.2 Hz), 7.94 (1H, d, J=7.9 Hz), 7.95 (2H, d, J=7.3 Hz), 8.09 (1H, d, J=8.5 Hz), 8.90 (1H, d, J=8.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 15.1, 26.8, 48.6, 52.1, 53.5, 116.1, 119.1, 123.3, 124.8, 127.2, 127.4 (2C), 128.2, 128.3 (3C), 129.9, 130.6, 131.5, 134.0, 136.3, 166.1, 168.3, 171.0. Anal. Calcd (found) for $C_{24}H_{22}N_2O_4$: C, 71.63 (71.80); H, 5.51 (5.34); N, 6.96% (6.59%).

4.4.14. 3-Benzoylamino-1-benzyl-3,4-dihydro-2(1*H*)-benzo[*f*]quinolinone (2i). Yield, 55% (conversion, 96%). Mp 194.0–195.0 °C. IR (KBr): 1640, 1690, 3090, 3340 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 3.37 (1H, dd, J=14.3, 14.3 Hz), 3.82 (1H, dd, J=6.4, 14.3 Hz), 5.06 (1H, ddd, J=6.4, 8.2, 14.3 Hz), 5.33 (1H, d, J=16.5 Hz), 5.37 (1H, d, J=16.5 Hz), 7.24–7.20 (1H, m), 7.34–7.28 (4H, m), 7.38 (1H, d, J=9.2 Hz), 7.44 (1H, dd, J=7.0, 7.0 Hz), 7.54 (2H, dd, J=7.0, 7.6 Hz), 7.56 (1H, dd, J=7.0, 7.6 Hz), 7.60 (1H, dd, J=7.6, 7.6 Hz), 7.80 (1H, d, J=9.2 Hz), 7.85 (1H, d, J=7.0 Hz), 8.00 (2H, d, J=7.0 Hz), 8.07 (1H, d, J=

7.6 Hz), 8.96 (1H, d, J=8.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.8, 45.4, 48.5, 116.4, 118.2, 123.2, 124.7, 126.5 (2C), 127.0, 127.1, 127.4 (2C), 128.0, 128.3, 128.4 (2C), 128.6 (2C), 129.7, 130.7, 131.5, 134.1, 136.1, 137.2, 166.3, 168.8. Anal. Calcd (found) for $C_{27}H_{22}N_2O_2$: C, 79.78 (79.95); H, 5.46 (5.55); N, 6.89% (6.99%).

4.4.15. 3-Benzoylamino-3,4-dihydro-1-methyl-2(1*H*)-benzo[*h*]quinolinone (2j). Yield, 35% (conversion, 72%). Mp 153.0–154.0 °C. IR (KBr): 1636, 1690, 3237 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.06–3.10 (1H, m), 3.30–3.36 (1H, m), 3.50 (3H, s), 4.73–4.78 (1H, m), 7.48 (1H, d, J=8.5 Hz), 7.53 (2H, dd, J=7.3, 7.3 Hz), 7.54 (1H, dd, J=7.3, 8.5 Hz), 7.56 (1H, dd, J=7.3, 8.6 Hz), 7.58 (1H, dd, J=7.3, 7.3 Hz), 7.75 (1H, d, J=8.6 Hz), 7.95 (1H, d, J=7.3 Hz), 7.97 (1H, d, J=8.5 Hz), 8.03 (1H, d, J=8.6 Hz), 8.74 (1H, d, J=7.9 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.6, 37.9, 49.2, 123.4, 124.8, 124.9, 125.3, 125.5, 125.7, 125.9, 127.3 (2C), 128.3 (2C), 128.6, 131.4, 133.8, 134.0, 136.5, 166.2, 171.1. Anal. Calcd (found) for $C_{21}H_{18}N_2O_2$: C, 76.34 (76.28); H, 5.49 (5.24); N, 8.48% (8.35%).

4.4.16. 3-(4-Anisoylamino)-3,4-dihydro-1-methyl-2(1*H*)-benzo[*h*]quinolinone (2k). Yield, 40% (conversion, 85%). Mp 224.0–225.0 °C. IR (KBr): 1660, 1680, 3400 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.07 (1H, dd, J=5.5, 15.6 Hz), 3.29–3.38 (1H, m), 3.50 (3H, s), 3.84 (3H, s), 4.75 (1H, ddd, J=5.5, 7.9, 14.2 Hz), 7.05 (2H, d, J=9.2 Hz), 7.47 (1H, d, J=8.5 Hz), 7.53 (1H, dd, J=7.9, 9.2 Hz), 7.57 (1H, dd, J=7.9, 8.5 Hz), 7.75 (1H, d, J=8.5 Hz), 7.94 (2H, d, J=9.2 Hz), 7.97 (1H, d, J=9.2 Hz), 8.02 (1H, d, J=8.5 Hz), 8.60 (1H, d, J=7.9 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.7, 37.8, 49.0, 55.3, 113.5 (2C), 123.3, 124.7, 124.8, 125.3, 125.4, 125.6, 125.8, 126.1, 128.6, 129.2 (2C), 133.7, 136.5, 161.7, 165.6, 171.3. Anal. Calcd (found) for $C_{22}H_{20}N_2O_3$: C, 73.32 (73.14); H, 5.59 (5.63); N, 7.77% (7.74%).

4.4.17. 3,4-Dihydro-3-(2,4-dimethoxybenzoylamino)-1-methyl-2(1*H*)-benzo[*h*]quinolinone (2l). Yield, 30% (conversion, 70%). Mp 198.0–198.5 °C. IR (KBr): 3360, 1672, 1639 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.07 (1H, dd, J=14.4, 15.1 Hz), 3.41 (1H, dd, J=5.5, 15.1 Hz), 3.52 (3H, s), 3.85 (3H, s), 4.00 (3H, s), 4.58 (1H, ddd, J=5.5, 5.5, 14.4 Hz), 6.69 (1H, dd, J=2.1, 8.3 Hz), 6.73 (1H, d, J=2.1 Hz), 7.49 (1H, d, J=8.3 Hz), 7.54 (1H, dd, J=6.9, 7.6 Hz), 7.57 (1H, dd, J=6.9, 8.3 Hz), 7.77 (1H, d, J=8.3 Hz), 7.95 (1H, d, J=8.3 Hz), 7.98 (1H, d, J=7.6 Hz), 8.01 (1H, d, J=8.3 Hz), 8.95 (1H, d, J=5.5 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 33.6, 39.5, 51.5, 57.2, 57.9, 100.3, 107.7, 115.2, 125.0, 126.5, 126.8, 126.9, 127.2, 127.4, 127.6, 130.3, 134.4, 135.4, 138.1, 160.7, 164.9, 165.3, 172.8. Anal. Calcd (found) for $C_{22}H_{22}N_2O_4$: C, 70.75 (70.76); H, 5.68 (5.95); N, 7.17% (7.22%).

4.4.18. *cis*-4-Methylaminocarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (3a). Yield, 5% (conversion, >99%). IR (KBr): 3244, 1651 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.03 (3H, d, J=4.9 Hz), 5.33 (1H, d, J=10.4 Hz), 6.80 (1H, d, J=10.4 Hz), 7.44 (1H, dd, J=7.3, 7.3 Hz), 7.47 (1H, d, J=7.3 Hz), 7.47 (1H, q, J=4.9 Hz), 7.53 (2H, m), 7.57 (2H, dd, J=7.3, 7.3 Hz), 7.65 (1H, dd, J=7.3, 7.3 Hz), 7.85 (1H, d, J=7.3 Hz), 7.92 (1H, d, J=7.3 Hz), 8.07 (2H, d, J=7.3 Hz), 8.07 (1H, d, J=7.3 Hz). ^{13}C NMR (500 MHz, DMSO-d_6): δ 25.0, 73.6, 80.2, 123.3, 123.8, 124.8, 125.5, 125.8, 127.1, 128.0, 128.2, 128.3 (2C), 128.6 (2C), 130.2, 132.0, 132.7, 132.9, 164.8, 167.9. EI-MS (m/z, %): 330 (M^+, 56.91).

4.4.19. *cis*-4-Aminocarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (3h). Yield, 3% (conversion, 94%). IR (KBr): 3453, 3321, 1667 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.32 (1H, d, J=10.4 Hz), 6.67 (1H, s), 6.76 (1H, d, J=10.4 Hz), 7.02 (1H, s), 7.45 (1H, dd, J=7.3, 7.9 Hz), 7.53–7.51 (3H, m), 7.56 (2H, dd, J=6.7, 7.9 Hz), 7.63 (1H, dd, J=7.9, 7.9 Hz), 7.84 (1H, d, J=7.9 Hz), 7.91 (1H, d, J=7.3 Hz), 8.05 (2H, d, J=6.7 Hz), 8.05 (1H, d, J=7.9 Hz). ^{13}C NMR (500 MHz, DMSO-d_6): δ 73.2, 80.3, 123.6, 124.1, 125.1, 125.6, 126.0, 127.2, 128.1, 128.3 (3C), 128.7 (2C), 130.3, 132.0, 132.9, 133.0, 164.6, 169.6. EI-MS (m/z, %): 316 (M^+, 48.36).

4.4.20. *cis*-4-Benzylaminocarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (3i). Yield, 10% (conversion, 96%). IR (KBr): 3265, 1657, 1645 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.77 (1H, dd, J=5.8, 15.3 Hz), 3.81 (1H, dd, J=6.1, 15.3 Hz), 5.47 (1H, d, J=10.7 Hz), 6.43 (2H, d, J=7.3 Hz), 6.83 (1H, d, J=10.7 Hz), 7.02 (2H, dd, J=7.0, 7.3 Hz), 7.07 (1H, dd, J=7.0, 7.0 Hz), 7.45 (1H, dd, J=7.6, 7.6 Hz), 7.59–7.53 (5H, m), 7.65 (1H, dd, J=7.3, 7.3 Hz), 7.90 (1H, d, J=7.6 Hz), 7.99–7.97 (1H, m), 8.08 (2H, d, J=8.6 Hz), 8.11–8.07 (1H, m), 8.13 (1H, dd, J=5.8, 6.1 Hz). ^{13}C NMR (500 MHz, DMSO-d_6): δ 41.6, 73.3, 80.4, 123.6, 123.9, 125.1, 125.6, 126.0, 126.2, 126.5 (2C), 127.1, 127.8 (2C), 128.1, 128.25 (2C), 128.3, 128.7 (2C), 130.2, 132.0, 132.6, 132.9, 137.6, 138.6, 164.7, 167.6. EI-MS (m/z, %): 406 (M^+, 32.06).

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