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meta-SUBSTITUENT EFFECTS ON THE PHOTOCYCLIZATION OF ARYL-SUBSTITUTED *N*-ACYL-□-DEHYDROALANINE DERIVATIVES

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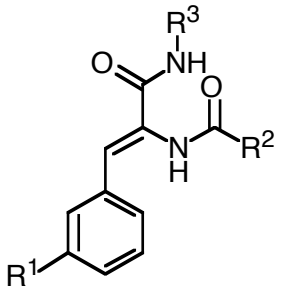
Abstract–On irradiation in methanol, the title compounds having chloro, trifluoromethyl or methyl group at the *meta* position on the styryl benzene ring gave 6-substituted (**2**) and 8-substituted (**3**) 1-methyl-3-(methylaminocarbonyl)isoquinolines along with 1-azetines. The preferential formation of **2** to **3** was explained in terms of steric effects on the cyclization process from the excited-state (*Z*)-isomer. The methoxy group introduced at the same *meta* position exerted dramatical electronic and steric effects on the excited-state cyclization pathway giving rise to regioselectively 6-substituted 2-quinolinone and isoquinoline derivatives. The 1-naphthyl substituent in the title compounds was found to have the same effects on the cyclization pathway as the methoxyphenyl group.

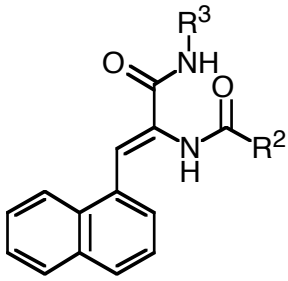
Photochemistry has continued to contribute to the development of efficient and selective transformations of organic materials into pharmaceutically important heterocyclic compounds.[1] In the course of our systematic study towards the characterization of the excited-state reactivities of *N*-acyl-□-dehydroamino acid derivatives, we have discovered some interesting photocyclization reactions in these dehydroamino acids.[2,3] One of the important findings is that the irradiation of substituted (*Z*)-*N*-acetyl-□-dehydrophenylalaninamides in polar solvents such as methanol and acetonitrile gives isoquinoline and 1-azetine derivatives in comparable yields[2a,c] while the selective formation of isoquinolines is observed when (*Z*)-*N*-acetyl-□-dehydrophenylalanine alkyl esters are irradiated under the same conditions.[2d] Interestingly, the replacement of the *N*-acetyl group by the substituted benzoyl system provided an excited-state reaction pathway that exclusively gives 1-azetine derivatives, owing to the steric bulkiness of the latter acyl group.[2b,c] Very recently, we found that 1-naphthyl-substituted *N*-acyl-□-dehydroamino acids in methanol containing triethylamine undergo an electron transfer-initiated photocyclization giving dihydrobenzoquinolinone derivatives with high selectivity and this cyclization reaction constitutes a new method for constructing the dihydrobenzoquinolinone skeleton.[3c]

The control of the excited-state reaction pathway of organic molecules by their substituents is one of the

most fascinating topics in the field of recent organic photochemistry.[4] In the photochemical solvolysis of methoxy-substituted benzyl acetates it has been found that *m*-methoxybenzyl acetate in the singlet excited state affords the heterolytic C–O bond cleavage products in addition to the products derived from the homolysis of this bond whereas only the latter products are obtained by the photolysis of *p*-methoxybenzyl acetate.[5] This novel substituent effect on the C–O bond cleavage mode was termed the "*meta* effect", the concept of which was introduced by Zimmmerman and his coworker.[5,6] Although there has been considerable mechanistic controversy concerning the heterolytic C–O bond cleavage mode,[6,7] it is an interesting extention of our study on the photocyclization of *N*-acyl-□-dehydroamino acid derivatives to control the cyclization pathway in the excited state utilizing the *meta*-substituent effects described above.[8] Taking into account that the photocyclization process of substituted □-dehydroamino acids undergoes great steric and electronic effects,[2,3] we designed and synthesized *N*-acyl-□-dehydro(*meta*-substituted phenyl)alanines (**1a**–**f**) and *N*-acyl-□-dehydro(1-naphthyl)alanines (**1g**–**j**) as related □-dehydroamino acid derivatives, and investigated substituent effects including the "*meta* effect" on the product distribution obtained by the irradiation of **1a**–**j** in methanol.

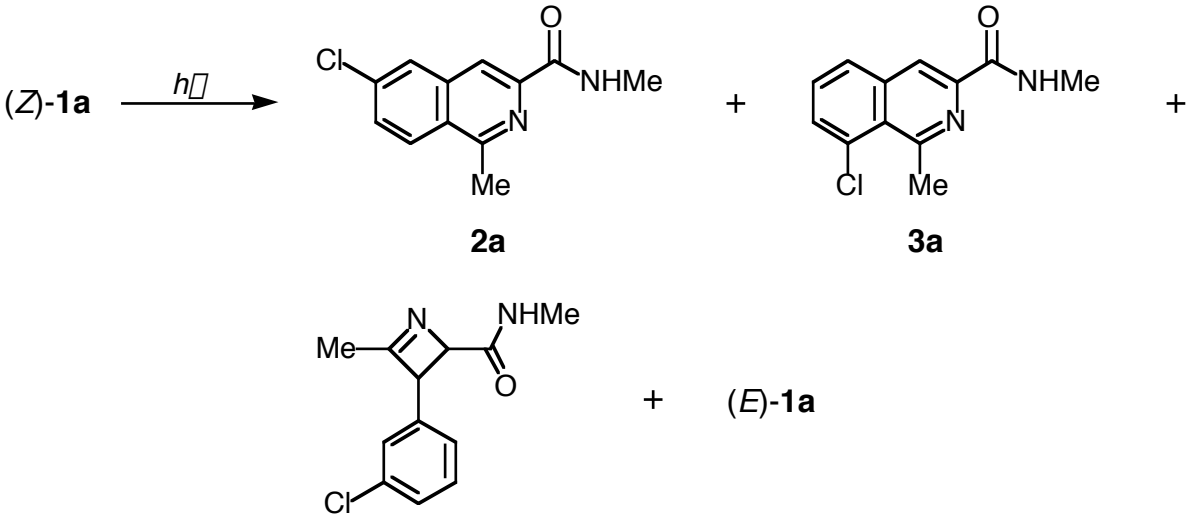


1a: R^1= Cl, R^2= R^3 = Me
1b: R^1= Cl, R^2= Me, R^3= CH_2Ph
1c: R^1= CF_3, R^2= R^3= Me
1d: R^1= Me, R^2= R^3= Me
1e: R^1= OMe, R^2= R^3= Me
1f: R^1= OMe, R^2= Ph, R^3= Me



1g: R^2= R^3 = Me
1h: R^2= Me, R^3= CH_2Ph
1i: R^2= Me, R^3= H
1j: R^2= Ph, R^3= Me

The starting (*Z*)-isomers (**1a**–**j**) were prepared in good yields by the ring-opening reactions of aryl-substituted oxazolones with primary amines in dry chloroform.[9] After a nitrogen purged methanol solution



(*Z*)-**1a** —*h*□→ **2a** + **3a** + **4a** (*trans* and *cis*) + (*E*)-**1a**

Scheme 1

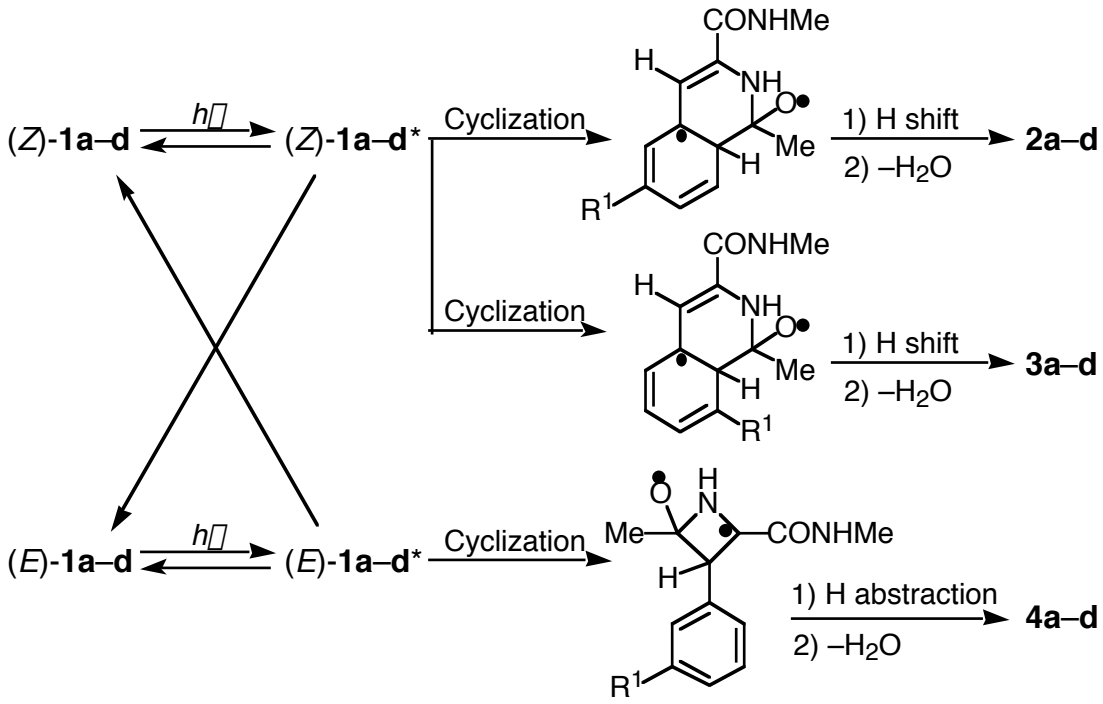
of **1a** (3.75×10^{-3} mol dm^{-3}, 250 mL) was irradiated with Pyrex filtered light (>280 nm) from a 400 W high pressure Hg lamp for 10 h at room temperature, the product mixture obtained was subjected to repeated preparative thin layer chromatography over silica gel, which allowed us to isolate (*Z*)-**1a**, (*E*)-**1a**, **2a**, **3a**, and *trans*-**4a** in 20, 6, 7, 4, and 3% yields, respectively (Scheme 1). The same product distribution was obtained also by the irradiation of (*Z*)-**1b**–**d**. 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. A careful ^{1}H NMR spectral analysis of the product mixture indicated the formation of detectable amounts of *cis*-**4**, the isolation of which was not successful owing to its poor yield. In addition, the ^{1}H NMR spectrum measured after 10 h irradiation indicated the occurrence of side reactions to some extent, while the products (**2**–**4**) were stable enough such that they undergo only negligible decomposition under the irradiation conditions. These findings make it possible to estimate the approximate composition of each compound by means of ^{1}H NMR spectroscopy, as shown in Table 1. The observation [that the overlap between NMR signals for proton at the 4-position in 6- and 8-substituted 1-methyl-3-(methylaminocarbonyl)isoquinolines is slight] allows us to evaluate their composition ratio. Thus, the results given in Table 1 clearly show that the 6-substituted isoquinoline isomer (**2**) is formed in preference to the 8-substituted isomer (**3**) and the isomer ratio (**2**/**3**) is estimated as about 2 irrespective of the substituents (Cl, CF_3, and Me) introduced. If we take a mechanism for formation of isoquinoline and 1-azetine derivatives (proposed in previous studies) into consideration (Scheme 2),[2] the preferential formation of the isomer (**2**) is explained on the basis of steric effects of these substituents on the cyclization process from the excited-state (*Z*)-isomer.

Table 1. Substituent effects on the composition of each compound obtained by the 10 h irradiation of the starting (*Z*)-**1a**–**d** in methanol at room temperature

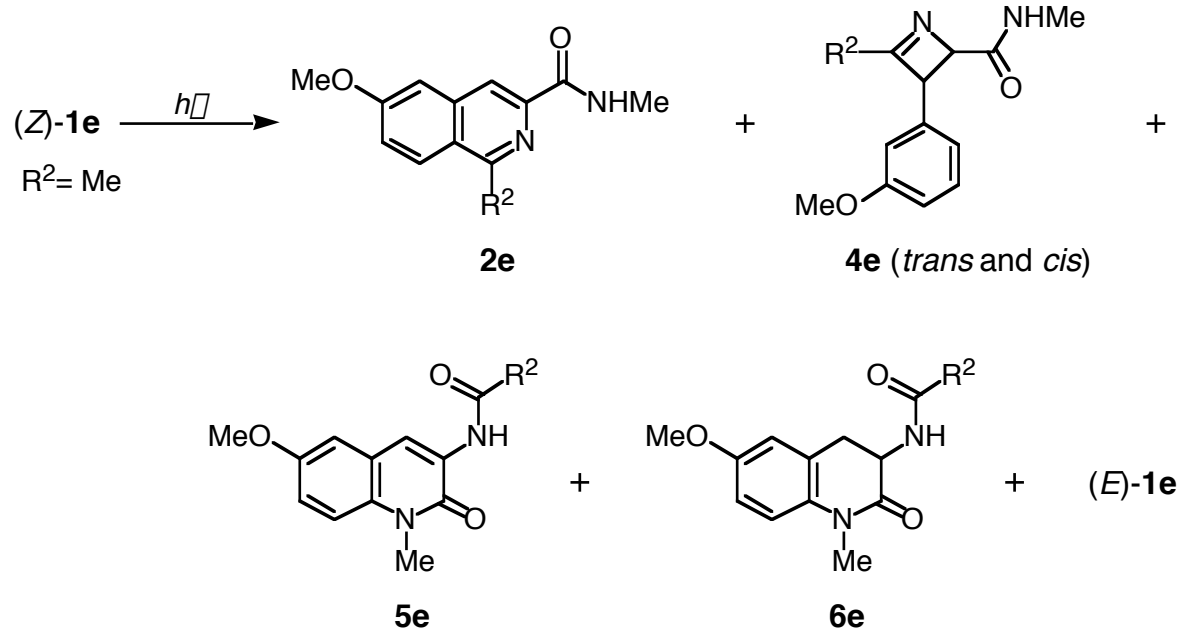
Compound	Composition (%)[a]					
	(*Z*)-**1**	(*E*)-**1**	**2**	**3**	*trans*-**4**	*cis*-**4**
(*Z*)-**1a**	39	15	12	8	24	2
(*Z*)-**1b**	40	17	11	6	23	3
(*Z*)-**1c**	48	13	12	7	17	3
(*Z*)-**1d**	41	27	13	6	10	3

a) The sum of composition for (*Z*)-**1**, (*E*)-**1**, **2**, **3**, and **4** was regarded as 100% for estimating approximate composition of each compound.

Interestingly, the 5 h irradiation of a nitrogen-purged methanol solution of **1e** (3.75×10^{-3} mol dm^{-3}, 250 mL) having the *meta*-methoxy group under the same conditions afforded **2e** (16%, isolated yield), *trans*-**4e** (6%), 6-methoxy-2-quinolinone (**5e**, 25%), and 3,4-dihydro-6-methoxy-2-quinolinone derivatives (**6e**,



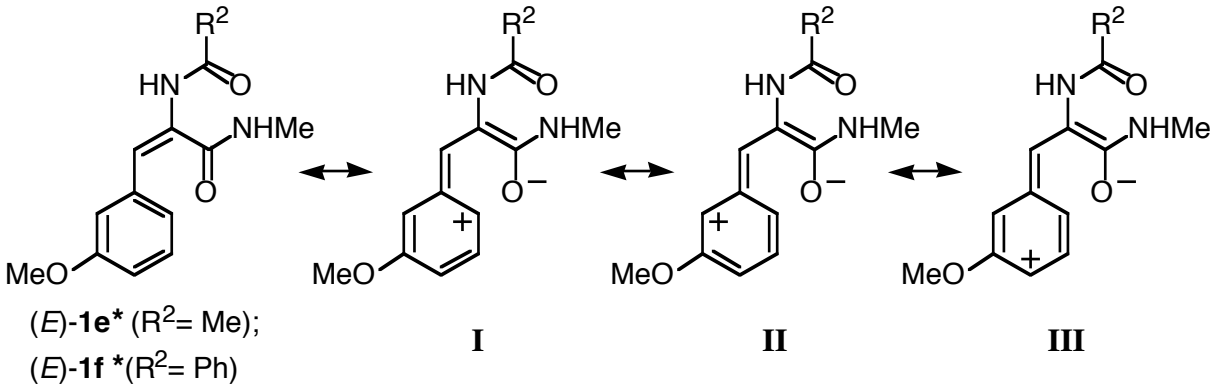
Scheme 2



Scheme 3

<1%) without forming any 8-methoxyquinolinone and isoquinoline isomers (Scheme 3). The structure of **5e** 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 8-position, (the signal of which appears at 7.28 ppm in chloroform-*d*), and the *N*-methyl protons giving their signal at 3.79 ppm. An examination of the ^{1}H NMR spectrum recorded after 5 h irradiation revealed that in addition to

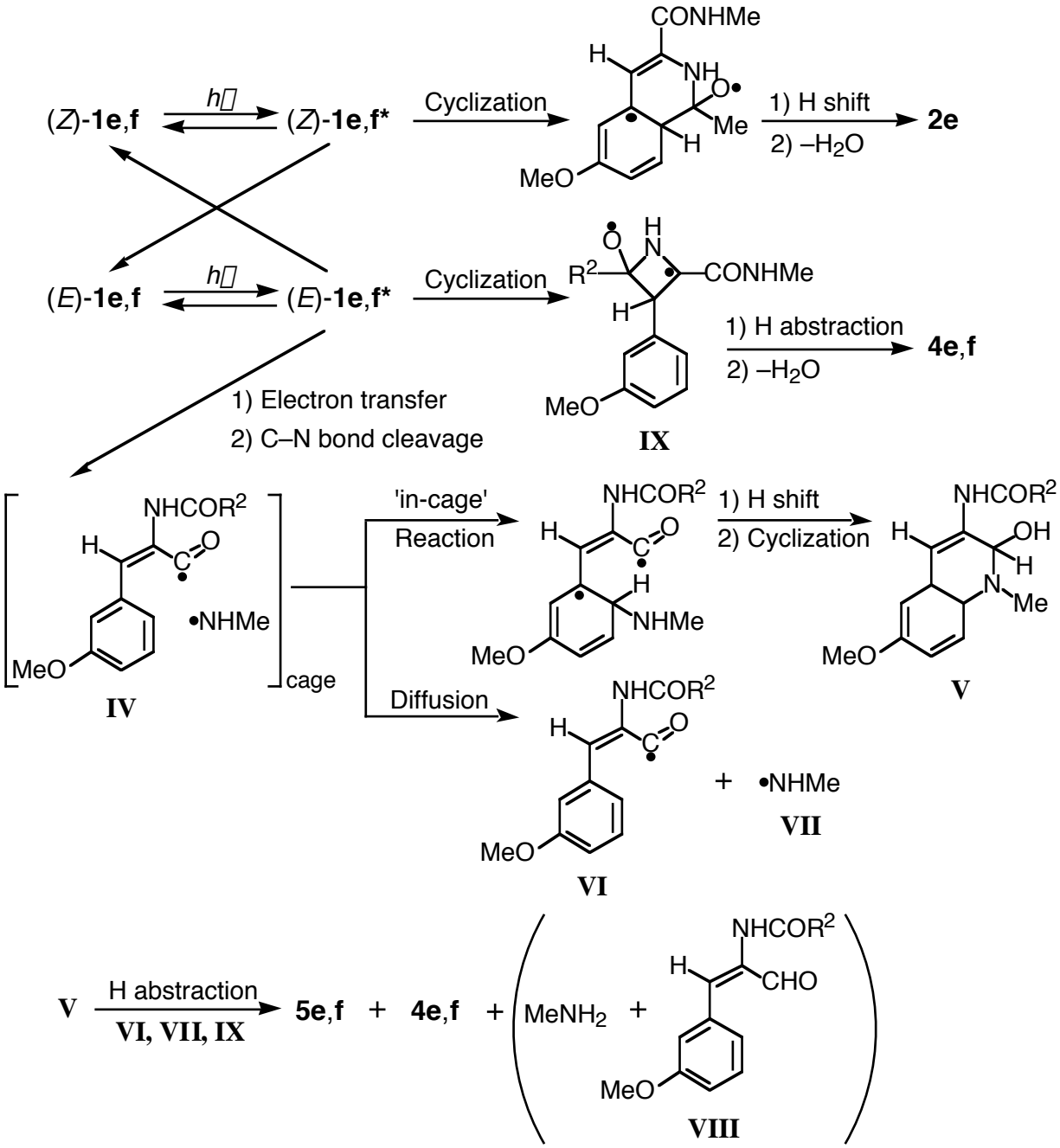
the signals assigned to small amounts of (*Z*)-**1e** and (*E*)-**1e** (the signal area ratio of **1e** to **5e** is 1:5), there are also signals (attributed to those of side reaction products), the area of which occupies approximately 20% of the total area; this proportion was estimated based on a given signal of each compound. Because the *para*-methoxy counterpart of **1e** has been shown to give the corresponding isoquinoline and 1-azetine derivatives on irradiation in methanol,[2a,c] the appearance of quinolinone derivative (**5e**) demonstrates that the presence of a strong electron-donating methoxy group at the *meta* position exerts a dramatic effect on the excited-state cyclization pathway. On the other hand, the starting (*Z*)-**1f** gave the corresponding quinolinone derivative (**5f**, R^2= Ph in Scheme 3) in 20% yield on irradiation for 10 h in nitrogen-purged methanol at room temperature, while the ^{1}H NMR spectrum of the reaction mixture indicated the presence of similar amounts of side reaction products along with (*Z*)-**1f**, (*E*)-**1f**, **4f** (*trans* + *cis*), and **5f** [composition ratio of these products, (*Z*)-**1f**: (*E*)-**1f**: **4f**: **5f**= 1.0: 0.9: 1.7: 2.3]. The ^{1}H NMR signals of **6f** (R^2= Ph in Scheme 3) could not be detected owing to strong overlap with those of by-products. As already demonstrated in our previous study,[2b,c] no formation of 6-substituted isoquinoline derivative (**2f**, R^2= Ph in Scheme 3) is due to the steric hindrance of the *N*-benzoyl group exerted in the cyclization process from the excited-state (*Z*)-isomer.



(*E*)-**1e*** (R^2= Me);
(*E*)-**1f ***(R^2= Ph)

Now we direct our attention to the formation mechanism of 2-quinolinone derivative (**5**). Though any attempts to isolate and characterize side reaction products were unsuccessful, the appearance of dihydroquinolinone derivative (**6e**) (that must be formed *via* electron transfer) strongly suggests the formation of an amine as one of the by-products.[3] This suggestion is supported by the finding that (*Z*)-**1e** (3.75×10^{-3} mol dm^{-3}) in methanol containing triethylamine (0.10 mol dm^{-3}) produces **6e** with high selectivity (78%) along with **2e** (13%) and **4e** (9%) without accompanying any side reactions under the same irradiation conditions (^{1}H NMR spectral analysis).[10] This finding demonstrates that the introduction of a methoxy group at the *meta* position greatly enhances the ability of the benzene ring to accept electron in the singlet excited state, and hence leads us to propose a pronounced contribution of the resonance structures (**I**, **II**, and **III**) in the excited state. These resonance structures suggest the occurrence of an efficient intramolecular electron transfer in **I** yielding the biradical which greatly promotes the homolytic C(=O)–NHMe bond cleavage, as shown in Scheme 4. Taking into account that **5** and **6** are formed *via* the excited-state (*E*)-isomer,[3c] we are allowed to assume the caged radical pair (**IV**). The 'in-cage' reaction gives the amino alcohol (**V**) while quinolinone derivative (**5**) is obtained by hydrogen

abstraction of the radicals (**VI**) and (**VII**) from **V**. In addition, methylamine and possibly the aldehyde (**VIII**) formed by this hydrogen abstraction may undergo secondary photoreactions affording by-products. It is likely that side reaction-derived radicals also participate in the hydrogen abstraction from **V** in addition to the biradical (**IX**), the precursor of **4**. The methoxy group attached at the *para* position may suppress intramolecular electron transfer described above by the conjugation of the methoxy-oxygen lone pair of electrons with the benzene ring having a positive charge.



Scheme 4

As already described, we observed regioselective photocyclizations of **1e** and **1f** that afford only the 6-

methoxy isoquinoline and quinolinone isomers but not 8-methoxy isomers. In order to confirm whether a methoxy group exerts large steric effects on the cyclization processes, conformational energies of (*Z*)-**1e** and (*E*)-**1e** were minimized by MM2 calculations (Figure 1). An examination of energy-minimized conformations reveals that the cyclization process taking place at the *ortho* position of the starting **1** experiences a great steric hindrance of the methoxy methyl hydrogens in any isomers. Therefore, we were led to conclude that the excited-state cyclization pathway undergoes dramatical electronic and steric effects of the *meta*-methoxy substituent.

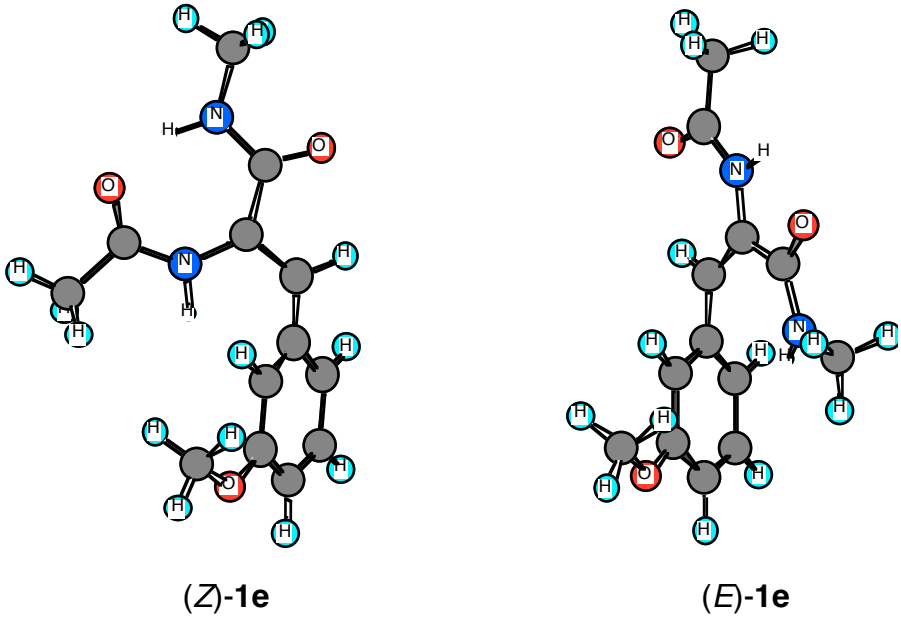
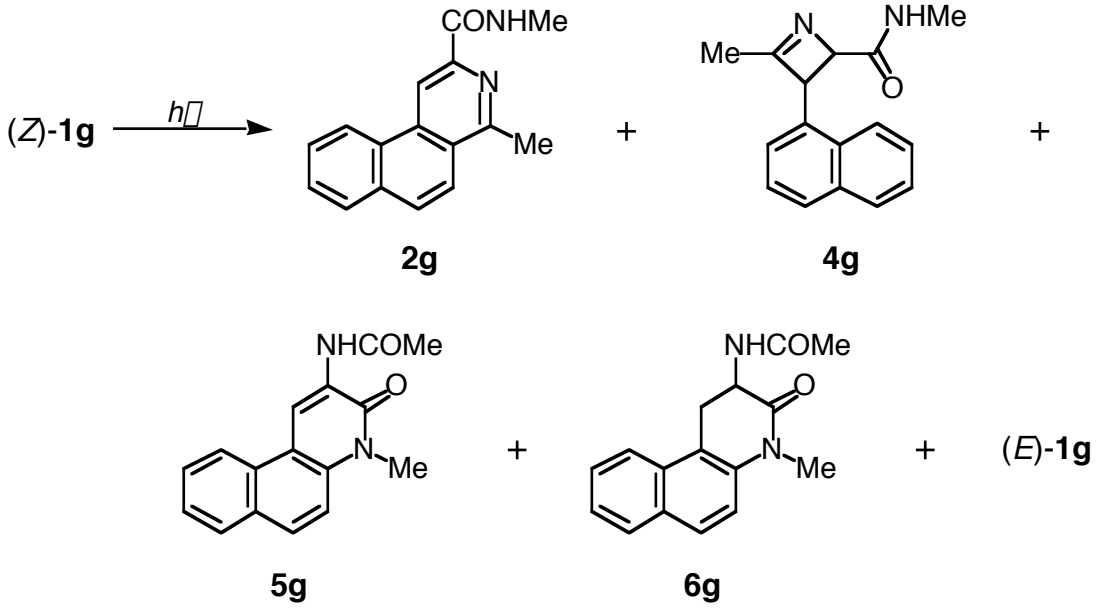


Figure 1. Energy-minimized conformations of (*Z*)-**1e** and (*E*)-**1e**

When a nitrogen-purged methanol solution of (*Z*)-**1g** (3.75×10^{-3} mol dm^{-3}, 250 mL) was irradiated with Pyrex filtered light for 5 h at room temperature, benzoquinolinone derivative (**5g**) was isolated in 25% yield in addition to (*Z*)-**1g** (10%), (*E*)-**1g** (10%), benzoisoquinoline (**2g**, 7%), and dihydrobenzoquinolinone derivatives (**6g**, 1%) (Scheme 5). 1-Azetine derivative (**4g**) could not be isolated because of its very minor formation. The ^{1}H NMR spectrum of the reaction mixture showed the presence of proton signals which cannot be assigned to those of the isolated products (about 30% of the total signal area). The appearance of **5g** as a major product establishes that a phenyl group fused to the benzene ring in **1e** (instead of a methoxy) also functions as one of the substituents that exhibit the so-called " *meta* effect" . The irradiation of (*Z*)-**1h**, (*Z*)-**1i**, and (*Z*)-**1j** under the same reaction conditions allowed us to isolate the corresponding benzoquinolinone derivative in 13 (**5h**), 17 (**5i**), and 16% (**5j**) yields, respectively. Thus, the observation of highly similar product distribution in the photocyclization of 1-naphthyl-substituted □-dehydroalanines confirms that benzoquinolinone derivatives are formed according to the same mechanism as that shown in Scheme 4. The large difference in product composition between (*Z*)-**1f** and (*Z*)-**1j** bearing the *N*-benzoyl group is that the latter derivative generates much smaller amounts of 1-azetine (**4j**) as compared to the former, implying that the introduction of the 1-naphthyl substituent in the place of the

para-methoxyphenyl significantly enhances the relative rate for the C(=O)–NHMe bond cleavage [in the excited-state (*E*)-isomer] leading to the caged radical pair (**IV**).



Scheme 5

EXPERIMENTAL

General

^{1}H and ^{13}C NMR and IR spectra were taken with a JEOL JNM-A500 spectrometer and a Hitachi 270-30 infrared spectrophotometer, respectively. Chemical shifts were determined using tetramethylsilane as an internal standard. Methanol was purified according to the standard procedure[11] and freshly distilled prior to use. All other reagents used were obtained from commercial sources and were of the highest grade available. MM2 calculations were accomplished by using CAChe 5.0 for Windows available from Fujitsu Ltd.[12]

General Procedure for the Synthesis of (*Z*)-2-Methyl-4-arylmethylene-5(4*H*)-oxazolones and (*Z*)-2-Phenyl-4-arylmethylene-5(4*H*)-oxazolones. *N*-Acylglycine (15.0 g, 0.13 mol), *meta*-substituted benzaldehyde (or 1-naphthaldehyde) (0.15 mol) and sodium acetate (8.0 g, 0.10 mol) were added to acetic anhydride (150 mL) and the resulting mixture was heated at 70–85 °C for 1–5 h with stirring. The mixture was cooled with ice and then poured into ice-water (200 mL). The solid separated out was collected by filtration with suction and washed with small amounts of cold ethanol. After the crude product had been air-dried at rt, it was recrystallized from chloroform–hexane to give yellow crystals (30–63%).

(*Z*)-2-Methyl-4-(3-chlorobenzylidene)-5(4*H*)-oxazolone: yield 52%; mp 112.0–113.0 °C; IR (KBr): 1797, 1659, 1263 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (3H, s), 7.03 (1H, s), 7.10–7.47 (2H,

m), 7.65–7.95 (1H, m), 8.16 (1H, s).

(*Z*)-2-Methyl-4-[3-(trifluoromethyl)benzylidene]-5(4*H*)-oxazolone: yield 47%; mp 123.5–124.5 °C; IR (KBr): 1792, 1662, 1262 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 2.44 (3H, s), 7.13 (1H, s), 7.57 (1H, dd, *J*= 7.6, 7.8 Hz), 7.67 (1H, d, *J*= 7.8 Hz), 8.23 (1H, d, *J*= 7.6 Hz), 8.39 (1H, s).

(*Z*)-2-Methyl-4-(3-methylbenzylidene)-5(4*H*)-oxazolone: yield 30%; mp 105.0–106.0 °C; IR (KBr): 1798, 1660, 1262 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 2.40 (6H, s), 7.11 (1H, s), 7.24 (1H, d, *J*= 7.3 Hz), 7.34 (1H, dd, *J*= 7.3, 7.8 Hz), 7.87 (1H, s), 7.89 (1H, d, *J*= 7.8 Hz).

(*Z*)-2-Methyl-(3-methoxybenzylidene)-5(4*H*)-oxazolone: yield 30%; mp 109.0–110.0 °C; IR (KBr): 1791, 1660, 1254 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 2.41 (3H, s), 3.86 (3H, s), 6.86 (1H, dd, *J*= 2.4, 8.1 Hz), 7.11 (1H, s), 7.35 (1H, dd, *J*= 7.6, 8.1 Hz), 7.59 (1H, d, *J*= 7.6 Hz), 7.75 (1H, d, *J*= 2.4 Hz).

(*Z*)-2-Phenyl-4-(3-methoxybenzylidene)-5(4*H*)-oxazolone: yield 63%; mp 103.5–104.0 °C; IR (KBr): 1800, 1659, 1200 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 3.84 (3H, s), 7.08 (1H, dd, *J*= 2.4, 7.8 Hz), 7.29 (1H, s), 7.43 (1H, dd, *J*= 7.8, 7.8 Hz), 7.63 (2H, dd, *J*= 7.1, 7.3 Hz), 7.73 (1H, dd, *J*= 7.1, 7.1 Hz), 7.83 (1H, d, *J*= 7.8 Hz), 7.93 (1H, d, *J*= 2.4 Hz), 8.09 (2H, d, *J*= 7.3 Hz).

(*Z*)-2-Methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone: yield 40%; mp 159.0–160.0 °C; IR (KBr): 1760, 1650, 1260 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 2.43 (3H, s), 7.54 (1H, dd, *J*= 7.3, 7.9 Hz), 7.58 (1H, dd, *J*= 7.3, 8.6 Hz), 7.61 (1H, dd, *J*= 7.3, 8.6 Hz), 7.88 (1H, d, *J*= 7.9 Hz), 7.93 (1H, d, *J*= 8.6 Hz), 8.02 (1H, s), 8.24 (1H, d, *J*= 8.6 Hz), 8.75 (1H, d, *J*= 7.3 Hz).

(*Z*)-2-Phenyl-4-(1-naphthylmethylene)-5-(4*H*)-oxazolone: yield 61%; mp 166.0–167.0 °C; IR (KBr): 1797, 1647, 1167 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 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).

General Procedure for the Synthesis of (*Z*)-2-Acylamino-*N*-alkyl-3-(3-substituted phenyl)-2-propenamides [(*Z*)-1a–f] and (*Z*)-2-Acylamino-*N*-alkyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1g–j]. (*Z*)-2-Methyl-4-arylmethylene-5(4*H*)-oxazolone or (*Z*)-2-phenyl-4-arylmethylene-5(4*H*)-oxazolone (0.020 mol) was added to dry chloroform (200 mL) containing alkylamine (0.021 mol) and the resulting solution was allowed to stand for several hours at rt or refluxed for 1 h. The reaction mixture was concentrated to dryness and the resulting residue was dissolved in ethanol (50 mL) and then treated with activated charcoal powder. After removal of the solvent under reduced pressure, the solid residue obtained was recrystallized from ethanol-hexane or ethyl acetate affording

colorless crystals (50–90%).

(*Z*)-2-Acetylamino-*N*-methyl-3-(3-chlorophenyl)-2-propenamide [(*Z*)-1a]: yield 87%; mp 196.0–198.0 °C (EtOH-hexane); IR (KBr): 3334, 1680 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s), 2.66 (3H, d, *J*= 4.3 Hz), 6.99 (1H, s), 7.36 (1H, d, *J*= 8.5 Hz), 7.40 (1H, dd, *J*= 7.3, 8.5 Hz), 7.46 (1H, d, *J*= 7.3 Hz), 7.56 (1H, s), 8.00 (H, q, *J*= 4.3 Hz), 9.44 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 26.3, 125.8, 127.9, 128.1, 128.6, 130.3, 131.4, 133.1, 136.5, 165.1, 169.3; *Anal.* Calcd for $C_{12}H_{13}N_2O_2Cl$: C, 57.04; H, 5.19; N, 11.09. Found: C, 56.61; H, 5.41; N, 10.83.

(*Z*)-2-Acetylamino-*N*-benzyl-3-(3-chlorophenyl)-2-propenamide [(*Z*)-1b]: yield 83%; mp 166.0–167.0 °C (EtOH-hexane); IR (KBr): 3220, 1650, 1629 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.01 (3H, s), 4.38 (2H, d, *J*= 5.5 Hz), 7.06 (1H, s), 7.21–7.25 (1H, m), 7.29–7.32 (4H, m), 7.38 (1H, d, *J*= 8.5 Hz), 7.42 (1H, dd, *J*= 7.3, 8.5 Hz), 7.50 (1H, d, *J*= 7.3 Hz), 7.61 (1H, s), 8.65 (1H, t, *J*= 5.5 Hz), 9.45 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 42.5, 126.1, 126.6, 127.1 (2C), 127.9, 128.1 (2C), 128.2, 128.7, 130.3, 131.5, 133.2, 136.5, 139.6, 164.8, 169.5; *Anal*. Calcd for $C_{18}H_{17}N_2O_2Cl$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.39; H, 5.59; N, 8.70.

(*Z*)-2-Acetylamino-*N*-methyl-3-[3-(trifluoromethyl)phenyl]-2-propenamide [(*Z*)-1c]: yield 62%; mp 163.0–163.5 °C (EtOH-hexane); IR (KBr): 3358, 1680, 1632 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s), 2.68 (3H, d, *J*= 4.3 Hz), 7.14 (1H, s), 7.62 (1H, dd, *J*= 7.3, 7.9 Hz), 7.66 (1H, d, *J*= 7.9 Hz), 7.79 (1H, d, *J*= 7.3 Hz), 7.85 (1H, s), 8.06 (1H, q, *J*= 4.3 Hz), 9.50 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.8, 26.3, 124.1 (q, *J*= 271 Hz), 124.7 (q, *J*= 4 Hz), 125.2 (q, *J*= 4 Hz), 125.9, 129.3 (q, *J*= 31 Hz), 129.6, 131.6, 133.2, 135.5, 165.0, 169.4; *Anal.* Calcd for $C_{13}H_{13}N_2O_2F_3$: C, 54.55; H, 4.58; N, 9.79. Found: C, 54.62; H, 4.59; N, 9.79.

(*Z*)-2-Acetylamino-*N*-methyl-3-(3-tolyl)-2-propenamide [(*Z*)-1d]: yield 73%; mp 184.0–184.5 °C (EtOH-hexane); IR (KBr): 3340, 1680, 1642 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 1.99 (3H, s), 2.30 (3H, s), 2.67 (3H, d, *J*= 4.3 Hz), 7.02 (1H, s), 7.14 (1H, d, *J*= 7.3 Hz), 7.27 (1H, dd, *J*= 7.3, 7.9 Hz), 7.32 (1H, d, *J*= 7.9 Hz), 7.33 (1H, s), 7.92 (1H, q, *J*= 4.3 Hz), 9.35 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 26.3, 56.0, 126.4, 127.8, 128.4, 129.1, 130.0 (2C), 134.1, 137.5, 165.4, 169.4; *Anal*. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 66.81; H, 7.18; N, 11.90.

(*Z*)-2-Acetylamino-*N*-methyl-3-(3-methoxyphenyl)-2-propenamide [(*Z*)-1e]: yield 50%; mp 159.0–160.0 °C (EtOH-hexane); IR (KBr): 3316, 1656 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 1.99 (3H, s), 2.66 (3H, d, *J*= 4.9 Hz), 3.76 (3H, s), 6.90 (1H, d, *J*= 7.9 Hz), 7.03 (1H, s), 7.10 (1H, d, *J*= 7.3 Hz), 7.13 (1H, s), 7.30 (1H, dd, *J*= 7.3, 7.9 Hz), 7.95 (1H, q, *J*= 4.9 Hz), 9.41 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 26.2, 55.0, 114.2, 114.4, 122.0, 127.5, 129.5, 130.3, 135.5, 159.1, 165.3, 169.3; *Anal.* Calcd for $C_{13}H_{16}N_2O_3$: C, 62.89; H, 6.50; N, 11.28. Found: C, 62.53; H, 6.71; N, 11.23.

(*Z*)-2-Benzoylamino-*N*-methyl-3-(3-methoxyphenyl)-2-propenamide [(*Z*)-1f]: yield 89%; mp 181.5–182.5 °C (EtOAc); IR (KBr): 3244, 1635 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): 2.69 (3H, d, *J*= 4.9 Hz), 3.59 (3H, s), 6.86 (1H, dd, *J*= 2.4, 7.3 Hz), 7.11 (1H, d, *J*= 7.9 Hz), 7.16 (1H, s), 7.27 (1H, d, *J*= 2.4 Hz), 7.28 (1H, dd, *J*= 7.9, 7.9 Hz), 7.51 (2H, dd, *J*= 7.3, 7.9 Hz), 7.58 (1H, dd, *J*= 7.3, 7.9 Hz), 8.02 (2H, d, *J*= 7.3 Hz), 8.08 (1H, q, *J*= 4.9 Hz), 9.91 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): 26.2, 54.7, 113.9, 114.5, 122.0, 127.8 (2C), 128.2 (2C), 128.9, 129.4, 130.2, 131.6, 133.5, 135.5, 159.0, 165.2, 165.7; *Anal*. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.76; H, 5.52; N, 8.81.

(*Z*)-2-Acetylamino-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1g]: yield 87%; mp 190.0–190.5 °C (EtOH-hexane); IR (KBr): 3340, 3236, 3180, 1644, 1628 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): 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): 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 for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.49; H, 5.73; N, 10.31.

(*Z*)-2-Acetylamino-*N*-benzyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1h]: yield 84%; mp 185.0–186.5 °C (EtOH-hexane); IR (KBr): 3280, 3230, 1650, 1630 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): 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): 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 for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.42; H, 5.75; N, 7.92.

(*Z*)-2-Acetylamino-3-(1-naphthyl)-2-propenamide [(*Z*)-1i]: yield 72%; mp 192.0–194.0 °C (EtOH-hexane); IR (KBr): 3364, 3264, 3210, 1647, 1610 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): 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): 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 for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.82; H, 5.17; N, 10.91.

(*Z*)-2-Benzoylamino-*N*-methyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1j]: yield 90%; mp 202.0–203.0 °C (EtOAc); IR (KBr): 3372, 3272, 1656, 1642 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): 2.75 (3H, d, *J*= 4.6 Hz), 7.42 (2H, dd, *J*= 7.3, 7.3 Hz), 7.43 (1H, dd, *J*= 7.0, 7.6 Hz), 7.53 (1H, dd, *J*= 7.3, 7.3 Hz), 7.54 (1H, dd, *J*= 6.6, 7.3 Hz), 7.56 (1H, dd, *J*= 6.6, 7.9 Hz), 7.61 (1H, d, *J*= 7.0 Hz), 7.75 (1H, s), 7.84 (1H, d, *J*= 7.6 Hz), 7.85 (2H, d, *J*= 7.3 Hz), 7.93 (1H, d, *J*= 7.3 Hz), 8.04 (1H, d, *J*= 7.9 Hz), 8.19 (1H, q, *J*= 4.6 Hz), 9.75 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): 26.3, 124.3, 125.3, 125.99, 126.02, 126.03, 126.4, 127.8 (2C), 128.1 (2C), 128.4 (2C), 131.1, 131.5 (2C), 132.4,

133.1, 133.8, 165.2, 166.2; *Anal*. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 75.97; H, 5.39; N, 8.45.

General Procedure for the Irradiation of (*Z*)-1a–j. A solution of (*Z*)-**1** (3.75×10^{-3} mol dm^{-3}) in methanol (250 mL), placed in a Pyrex vessel, was irradiated for a given period of time under nitrogen with Pyrex-filtered light from a 400 W high pressure Hg lamp at rt. At a given irradiation time, an appropriate amount of the solution (5 mL) was pipetted off and concentrated to dryness *in vacuo* giving the residue which was subjected to ^{1}H NMR spectral analysis in dimethyl-d_6 sulfoxide. The composition was estimated from the area ratio of a given ^{1}H NMR signal for each compound. The remaining solution was concentrated to dryness under reduced pressure and the resulting residue was subjected to preparative thin-layer chromatography over silica gel (developing solvent: ethyl acetate-hexane or ethyl acetate-chloroform). For the purpose of isolating and purifying the photoproducts, column chromatography over silica gel (230 mesh, Merck) was also used. The separation of isoquinoline isomers (**2** and **3**) from their mixture was effected by fractional crystallization from ethyl acetate followed by preparative thin-layer chromatography over silica gel (developing solvent: ethyl acetate-hexane). However, the isoquinoline isomer (**2d** and **3a–c**) of higher solubility was contaminated with small amounts of the isomer (**3d** and **2a–c**), the removal of which was very difficult. Physical and spectroscopic properties of the (*E*)-isomers, isoquinolines (**2** and **3**), 1-azetines (**4**), quinolinones (**5**), and dihydroquinolinones (**6**) isolated are as follows.

(*E*)-1a: yield 6%; mp 161.0–162.0 °C (EtOAc); IR (KBr): 3311, 3275, 1655, 1620 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.94 (3H, s), 2.53 (3H, d, *J*= 4.8 Hz), 6.75 (1H, s), 7.12 (1H, d, *J*= 7.6 Hz), 7.22 (1H, d, *J*= 8.2 Hz), 7.22 (1H, s), 7.28 (1H, dd, *J*= 7.6, 8.2 Hz), 8.11 (1H, q, *J*= 4.8 Hz), 9.71 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.4, 25.8, 113.2, 126.3, 126.4, 127.1, 129.9, 132.8, 134.9, 137.7, 165.0, 170.0.

(*E*)-1e: yield 8%; mp 140.0–140.5 °C (EtOAc); IR (KBr): 3335, 3065, 1686, 1622 cm^{-1}; ^{1}H NMR (500 MHz, DMSO- d_6): δ 1.94 (3H, s), 2.54 (3H, d, *J*= 4.8 Hz), 3.71 (3H, s), 6.75 (1H, dd, *J*= 2.7, 8.2 Hz), 6.77 (1H, d, *J*= 7.6 Hz), 6.77 (1H, s), 6.79 (1H, d, *J*= 2.7 Hz), 7.17 (1H, dd, *J*= 7.6, 8.2 Hz), 8.04 (1H, q, *J*= 4.8 Hz), 9.61 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 23.4, 25.8, 54.9, 112.3, 112.8, 114.5, 120.4, 129.1, 133.7, 136.7, 159.0, 165.3, 168.2.

(*E*)-1g: yield 10%; mp 167.5–168.5 °C (EtOAc); 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.

6-Chloro-3-methylaminocarbonyl-1-methylisoquinoline (2a): yield 7%; mp 167.0–168.0 °C (EtOAc); IR (KBr): 3408, 1674, 1618 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.89 (3H, d, J= 4.9 Hz), 2.96 (3H, s), 7.79 (1H, dd, J= 2.4, 8.6 Hz), 8.32 (1H, d, J= 8.6 Hz), 8.33 (1H, d, J= 2.4 Hz), 8.38 (1H, s), 8.80 (1H, q, J= 4.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.1, 26.0, 117.2, 126.1, 127.2, 128.3, 129.1, 135.5, 136.7, 143.5, 158.0, 164.3; *Anal.* Calcd for $C_{12}H_{11}N_2OCl$: C, 61.41; H, 4.72; N, 11.94. Found: C, 61.44; H, 4.44; N, 12.31.

3-Benzylaminocarbonyl-6-chloro-1-methylisoquinoline (2b): yield 6%; mp 174.0–175.0 °C (EtOAc); IR (KBr): 3394, 1668, 1617 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.97 (3H, s), 4.57 (2H, d, J= 6.1 Hz), 7.25 (1H, dd, J= 7.3, 7.3 Hz), 7.33 (2H, dd, J= 7.3, 7.9 Hz), 7.36 (2H, d, J= 7.9 Hz), 7.79 (1H, dd, J= 2.4, 8.9 Hz), 8.33 (1H, d, J= 8.9 Hz), 8.33 (1H, d, J= 2.4 Hz), 8.41 (1H, s), 9.34 (1H, t, J= 6.1 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.2, 42.5, 117.8, 126.3, 126.8, 127.3, 127.4 (2C), 128.3, 128.5 (2C), 129.3, 135.7, 136.7, 139.6, 143.5, 158.2, 164.0; *Anal.* Calcd for $C_{18}H_{15}N_2OCl$: C, 69.57; H, 4.86; N, 9.01. Found: C, 69.61; H, 4.57; N, 8.71.

3-Methylaminocarbonyl-1-methyl-6-trifluoromethylisoquinoline (2c): yield 5%; mp 190.0–191.0 °C (EtOAc); IR (KBr): 3412, 1668, 1617 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.90 (3H, d, J= 4.9 Hz), 3.03 (3H, s), 8.02 (1H, dd, J= 1.8, 8.5 Hz), 8.52 (1H, d, J= 8.5 Hz), 8.59 (1H, s), 8.71 (1H, d, J= 1.8 Hz), 8.86 (1H, q, J= 4.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.1, 26.0, 118.7, 123.9 (q, J= 273 Hz), 124.0 (q, J= 4 Hz), 126.6 (q, J= 4 Hz), 128.0, 128.9, 130.6 (q, J= 31 Hz), 135.1, 143.9, 158.4, 164.3; *Anal*. Calcd for $C_{13}H_{11}N_2OF_3$: C, 58.21; H, 4.13; N, 10.44. Found: C, 58.49; H, 3.74; N, 10.26.

1,6-Dimethyl-3-methylaminocarbonylisoquinoline (2d): yield 5%; oily liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 2.53 (3H, s), 2.88 (3H, d, J= 4.6 Hz), 2.93 (3H, s), 7.61 (1H, dd, J= 1.7, 8.6 Hz), 7.91 (1H, d, J= 1.7 Hz), 8.18 (1H, d, J= 8.6 Hz), 8.26 (1H, s), 8.73 (1H, q, J= 4.6 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 21.3, 22.1, 26.0, 117.5, 125.8, 126.2, 127.4, 130.8, 135.8, 140.9, 142.7, 157.4, 164.7.

6-Methoxy-1-methyl-3-methylaminocarbonylisoquinoline (2e): yield 16%; mp 192.0–193.0 °C (EtOAc); IR (KBr): 3418, 1671, 1623 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.87 (3H, d, J= 4.9 Hz), 2.88 (3H, s), 3.81 (3H, s), 7.13 (1H, dd, J= 2.6, 9.2 Hz), 7.54 (1H, d, J= 2.6 Hz), 8.16 (1H, d, J= 9.2 Hz), 8.26 (1H, s), 8.69 (1H, q, J= 4.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.0, 26.0, 55.6, 106.8, 117.5, 120.8, 123.4, 127.8, 137.9, 143.1, 157.0, 160.6, 164.8; *Anal.* Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.38. Found: C, 67.61; H, 6.19; N, 12.38.

1-Methyl-3-methylaminocarbonylbenzo[*f*]isoquinoline (2g): yield 7%; mp 135.0–136.0 °C (EtOAc-hexane); IR (KBr): 3406, 1659 cm^{-1}; ^1H 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): 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 for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.69; H, 5.71; N, 11.37.

3-Benzylaminocarbonyl-1-methylbenzo[*f*]isoquinoline (2h): yield 12%; mp 147.0–148.0 °C (EtOAc-hexane); IR (KBr): 3394, 1674 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): 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): 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 for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 81.05; H, 5.47; N, 8.70.

3-Aminocarbonyl-1-methylbenzo[*f*]isoquinoline (2i): yield 8%; mp 254.0–255.5 ℃ (EtOAc); IR (KBr): 3442, 1683 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): 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): 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 for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.96; H, 5.02; N, 11.79.

8-Chloro-3-methylaminocarbonyl-1-methylisoquinoline (3a): yield 4%; oily liquid; ^{1}H NMR (500 MHz, DMSO-d_6): 2.91 (3H, d, *J*= 4.9 Hz), 2.95 (3H, s), 7.74 (1H, dd, *J*= 7.3, 7.9 Hz), 7.86 (1H, d, *J*= 7.3 Hz), 8.15 (1H, d, *J*= 7.9 Hz), 8.40 (1H, s), 8.81 (1H, q, *J*= 4.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): 22.1, 26.0, 117.2, 126.1, 127.2, 128.3, 129.1, 135.5, 136.7, 143.5, 158.0, 164.3.

3-Benzylaminocarbonyl-8-chloro-1-methylisoquinoline (3b): yield 3%; oily liquid; ^{1}H NMR (500 MHz, DMSO-d_6): 3.28 (3H, s), 4.58 (2H, d, *J*= 6.7 Hz), 7.25 (1H, dd, *J*= 7.3, 7.3 Hz), 7.33 (2H, dd, *J*= 7.3, 7.9 Hz), 7.36 (2H, d, *J*= 7.9 Hz), 7.75 (1H, dd, *J*= 7.9, 7.9 Hz), 7.89 (1H, dd, *J*= 1,2, 7.9 Hz), 8.17 (1H, dd, *J*= 1.2, 7.9 Hz), 8.45 (1H, s), 9.39 (1H, t, *J*= 6.7 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): 29.1, 42.4, 119.2, 125.9, 126.8, 127.4 (2C), 128.3 (2C), 129.0, 130.8, 131.1, 131.9, 139.0, 139.6, 142.4, 156.8, 163.7.

3-Methylaminocarbonyl-1-methyl-8-trifluoromethylisoquinoline (3c): yield 2%; oily liquid; ^{1}H NMR (500 MHz, DMSO-d_6): 2.91 (3H, d, *J*= 4.9 Hz), 3.08 (3H, s), 8.02 (1H, dd, *J*= 7.3, 7.9 Hz), 8.31 (1H, d, *J*= 7.9 Hz), 8.52 (1H, s), 8.53 (1H, d, *J*= 7.3 Hz), 8.88 (1H, q, *J*= 4.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): 26.0, 26.6, 118.8, 124.1, 124.17 (q, *J*= 31 Hz), 124.21 (q, *J*= 273 Hz), 129.1, 129.8 (q, *J*= 8 Hz), 135.3, 138.6, 142.7, 154.7, 163.9.

1,8-Dimethyl-3-methylaminocarbonylisoquinoline (3d): yield 3%; mp 155.0–156.0 °C (EtOAc-

hexane); IR (KBr): 3391, 1670, 1665 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.88 (3H, *d*, J= 4.6 Hz), 2.95 (3H, s), 3.16 (3H, s), 7.55 (1H, d, *J*= 7.6 Hz), 7.64 (1H, dd, *J*= 7.6, 8.0 Hz), 7.97 (1H, d, *J*= 8.0 Hz), 8.29 (1H, s), 8.76 (1H, q, *J*= 4.6 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 25.0, 26.0, 29.0, 118.8, 127.5, 128.7, 130.1, 132.0, 136.5, 137.8, 141.5, 157.9, 164.5; *Anal.* Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.76; H, 6.65; N, 13.19.

We succeeded in isolating *trans*-**4a**, **4b**, **4d**, and **4e** whose ^1H NMR spectra were consistent with the proposed structure, although the *trans*-isomers were contaminated with small amounts of byproducts and/or the azetine-derived decomposition products.

***trans*-3-(3-Chlorophenyl)-2-methyl-4-methylaminocarbonyl-1-azetine (*trans*-4a):** yield 3%; oily liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 2.07 (3H, d, *J*= 1.2 Hz), 2.64 (3H, d, *J*= 4.3 Hz), 4.33 (1H, dd, *J*= 1.2, 7.3 Hz), 5.53 (1H, d, *J*= 7.3 Hz), 7.30 (1H, d, *J*= 7.3 Hz), 7.38 (1H, s), 7.41 (1H, d, *J*= 7.9 Hz), 7.44 (1H, dd, *J*= 7.3, 7.9 Hz), 7.87 (1H, q, *J*= 4.3 Hz).

***trans*-4-Benzylaminocarbonyl-3-(3-chlorophenyl)-2-methyl-1-azetine (*trans*-4b):** yield 4%; oily liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 2.09 (3H, s), 4.28–4.37 (2H, m), 4.44 (1H, d, *J*= 7.3 Hz), 5.57 (1H, d, *J*= 7.3 Hz), 7.24 (1H, dd, *J*= 7.3, 7.3 Hz), 7.27 (2H, d, *J*= 7.9 Hz), 7.30 (1H, d, *J*= 7.0 Hz), 7.32 (2H, dd, *J*= 7.3, 7.9 Hz), 7.39 (1H, s), 7.41 (1H, d, *J*= 8.5 Hz), 7.45 (1H, dd, *J*= 7.0, 8.5 Hz), 8.45–8.55 (1H, m).

***trans*-2-Methyl-4-methylaminocarbonyl-3-(3-tolyl)-1-azetine (*trans*-4d):** yield 2%; oily liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 2.06 (3H, d, *J*= 1.2 Hz), 2.31 (3H, s), 2.64 (3H, d, *J*= 4.3 Hz), 4.30 (1H, dd, *J*= 1.2, 7.3 Hz), 5.47 (1H, d, *J*= 7.3 Hz), 7.09 (1H, d, *J*= 7.9 Hz), 7.12 (1H, s), 7.15 (1H, d, *J*= 7.9 Hz), 7.28 (1H, dd, *J*= 7.9, 7.9 Hz), 7.86 (1H, q, *J*= 4.3 Hz).

***trans*-3-(3-Methoxyphenyl)-2-methyl-4-methylaminocarbonyl-1-azetine (*trans*-4e):** yield 6%; oily liquid; ^1H NMR (500 MHz, DMSO-d_6): δ 2.06 (3H, s), 2.64 (3H, d, *J*= 4.3 Hz), 3.76 (3H, s), 4.31 (1H, d, *J*= 7.3 Hz), 5.48 (1H, d, *J*= 7.3 Hz), 6.19–6.84 (3H, m), 7.32 (1H, dd, *J*= 7.9, 7.9 Hz), 7.87 (1H, q, *J*= 4.3 Hz).

3-Acetylamino-6-methoxy-1-methyl-2(1*H*)-quinolinone (5e): yield 25%; mp 174.0–175.0 °C (EtOAc); IR (KBr): 3310, 1689, 1626 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.19 (3H, s), 3.70 (3H, s), 3.81 (3H, s), 7.13 (1H, dd, *J*= 2.6, 9.2 Hz), 7.45 (1H, d, *J*= 9.2 Hz), 7.54 (1H, d, *J*= 2.6 Hz), 8.61 (1H, s), 9.42 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 24.2, 30.1, 55.5, 110.0, 115.8, 116.9, 119.5, 121.1, 128.4, 129.9, 154.8, 156.4, 169.7; *Anal.* Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.71; N, 11.38. Found: C, 62.97; H, 5.73; N, 11.41.

3-Benzoylamino-6-methoxy-1-methyl-2(1*H*)-quinolinone (5f): yield 20%; mp 198.0–198.5 °C

(EtOAc); IR (KBr): 3368, 1666, 1638 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 3.65 (3H, s), 3.86 (3H, s), 7.30 (1H, d, *J*= 2.8, 7.2 Hz), 7.46 (1H, d, *J*= 2.8 Hz), 7.52 (1H, d, *J*= 7.2 Hz), 7.56 (2H, dd, *J*= 7.3, 7.6 Hz), 7.64 (1H, dd, *J*= 7.6, 7.6 Hz), 8.04 (2H, d, *J*= 7.3 Hz), 9.65 (1H, s), 11.54 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 30.2, 55.4, 110.2, 116.0, 117.3, 120.1, 120.9, 127.0 (2C), 127.7, 128.9 (2C), 130.0, 132.2, 133.7, 154.9, 156.6, 164.9; *Anal.* Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.19; H, 5.44; N, 9.26.

3-Acetylamino-1-methyl-2(1*H*)-benzo[*f*]quinolinone (5g): yield 25%; mp 208.0–208.5 °C (EtOAc-hexane); IR (KBr): 3316, 1680, 1605 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.25 (3H, s), 3.88 (3H, s), 7.58 (1H, d, *J*= 6.7, 7.3 Hz), 7.73 (1H, dd, *J*= 6.7, 8.5 Hz), 7.81 (1H, d, *J*= 9.2 Hz), 8.02 (1H, d, *J*= 7.3 Hz), 8.07 (1H, d, *J*= 9.2 Hz), 8.30 (1H, d, *J*= 8.5 Hz), 9.58 (1H, s), 9.61 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 24.3, 30.7, 113.8, 115.3, 115.4, 121.5, 125.4, 127.8, 128.2, 128.7, 128.9, 129.1, 129.5 134.0, 156.7, 170.1; *Anal.* Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.47; H, 5.02; N, 10.63.

3-Acetylamino-1-benzyl-2(1*H*)-benzo[*f*]quinolinone (5h): yield 13%; mp 264.0–265.0 °C (EtOAc-hexane); IR (KBr): 3320, 1653, 1636 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.27 (3H, s), 5.80 (2H, s), 7.23 (2H, d, *J*= 7.3 Hz), 7.25 (1H, dd, *J*= 7.3, 7.3 Hz), 7.32 (2H, dd, *J*= 7.3, 7.3 Hz), 7.57 (1H, dd, *J*= 7.3, 7.3 Hz), 7.65 (1H, d, *J*= 9.7 Hz), 7.74 (1H, dd, *J*= 7.3, 7.3 Hz), 7.96 (1H, d, *J*= 7.3 Hz), 7.96 (1H, d, *J*= 9.7 Hz), 8.33 (1H, d, *J*= 7.3 Hz), 9.69 (1H, s), 9.75 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 24.2, 45.9, 114.2, 115.5, 116.0, 121.5, 125.4, 126.4 (2C), 127.1, 127.8, 128.2, 128.5, 128.6 (2C), 128.9, 129.0, 129.5, 133.2, 136.5, 156.9, 170.1; *Anal.* Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.83; H, 5.43; N, 8.56.

3-Acetylamino-2(1*H*)-benzo[*f*]quinolinone (5i): yield 17%; mp 330.0–331.0 °C (EtOAc); IR (KBr): 3320, 1658, 1636 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 2.23 (3H, s), 7.49 (1H, d, *J*= 8.5 Hz), 7.54 (1H, dd, *J*= 7.3, 8.6 Hz), 7.70 (1H, dd, *J*= 7.3, 7.9 Hz), 7.95 (1H, d, *J*= 8.5 Hz), 7.96 (1H, d, *J*= 8.6 Hz), 8.25 (1H, d, *J*= 7.9 Hz), 9.53 (1H, s), 9.58 (1H, s), 12.59 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 24.2, 113.0, 116.0, 116.4, 121.3, 125.0, 127.6, 128.8, 128.9, 129.0, 129.2, 129.3, 132.8, 157.1, 169.9; *Anal.* Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 71.48; H, 4.61; N, 11.06.

3-Benzoylamino-1-methyl-2(1*H*)-benzo[*f*]quinolinone (5j): yield 16%; mp 246.0–246.5 °C (EtOH); IR (KBr): 3372, 1678, 1644 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ 3.94 (3H, s), 7.62 (1H, dd, *J*= 7.9, 7.9 Hz), 7.62 (2H, dd, *J*= 7.3, 7.9 Hz), 7.68 (1H, dd, *J*= 7.9, 7.9 Hz), 7.77 (1H, dd, *J*= 7.9, 7.9 Hz), 7.88 (1H, d, *J*= 9.1 Hz), 8.02 (2H, d, *J*= 7.3 Hz), 8.06 (1H, d, *J*= 7.9 Hz), 8.14 (1H, d, *J*= 9.1 Hz), 8.44 (1H, d, *J*= 7.9 Hz), 9.65 (1H, s), 9.68 (1H, s); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 31.0, 113.9, 115.4, 116.4, 121.7, 125.6, 127.2 (2C), 127.6, 128.0, 128.8, 129.0 (2C), 129.2, 130.1, 132.4, 133.8, 134.4, 157.1, 165.4; *Anal*. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C,

76.77; H, 5.08; N, 8.50.

3-Acetylamino-3,4-dihydro-6-methoxy-1-methyl-2(1*H*)-quinolinone (6e): amorphous solid; yield <1%; ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.90 (3H, s), 2.84 (1H, dd, J= 14.0, 14.6 Hz), 2.97 (1H, dd, J= 6.1, 14.6 Hz), 3.26 (3H, s), 3.74 (3H, s), 4.40 (1H, ddd, *J*= 6.1, 7.9, 14.0 Hz), 6.86 (1H, dd, *J*= 3.0, 8.5 Hz), 6.88 (1H, d, *J*= 3.0 Hz), 7.04 (1H, d, *J*= 8.5 Hz), 8.18 (1H, d, *J*= 7.9 Hz); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.5, 29.8, 31.3, 48.1, 55.2, 112.4, 113.7, 116.1, 125.5, 133.0, 154.8, 167.6, 169.1. These spectral data were consistent with the 3,4-dihydro form of 2-quinolinone derivative (**5e**).

3-Acetylamino-3,4-dihydro-1-methyl-2(1*H*)-benzo[*f*]quinolinone (6g): yield 1%; mp 231.5–232.5 °C (EtOAc); ^{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. These spectral data were consistent with the 3,4-dihydro form of benzoquinolinone derivative (**5g**).

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