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ELECTRON TRANSFER-INITIATED AND HIGHLY SELECTIVE PHOTOCYCLIZATION OF *N*-ACYL-α-DEHYDROARYLALANINAMIDES TO 3,4-DIHYDROQUINOLINONE DERIVATIVES

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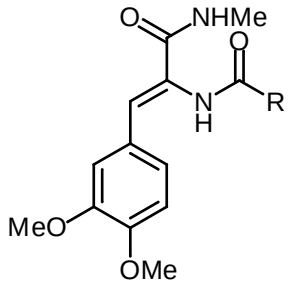
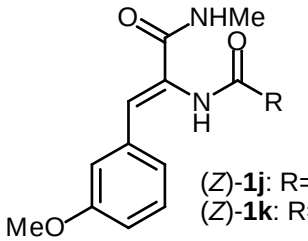
Abstract–The irradiation of (*Z*)-*N*-acyl-α-dehydroarylalaninamides [(*Z*)-**1**] in methanol containing 1,8-diazabicyclo[5.4.0]undec-7-ene gave substituted 3,4-dihydro-2-quinolinones (**2**) in high yields along with minor amounts of 2-quinolinone (**3**) and 4,5-dihydrooxazole (**4**) derivatives. Analysis of substituent and tertiary amine base effects on the selectivity of each product showed that **2** and **4** are formed *via* electron transfer from the amine to the excited-state (*E*)-**1**, the cyclization of which proceeds in competition with this electron transfer to afford **3**.

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 biologically active natural products. Many useful synthetic methods of 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 substituted 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 *N*-acyl-α-dehydroamino acids.[5–8] In the course of this study we discovered novel intramolecular and intermolecular ET-initiated photocyclization reactions of substituted *N*-acyl-α-dehydronaphthylalaninamides that afford the corresponding 3,4-dihydrobenzo[*f*]quinolinones.[6] Because many heterocyclic compounds having a dihydroquinolinone ring exhibit pharmacological and physiological activities,[9] it is of great significance to develop synthetic methods for the construction of this quinolinone ring. Very recently we found that the PET reaction of *N*-(2,4-dimethoxybenzoyl)-α-dehydronaphthylalaninamide affords selectively the corresponding dihydrobenzoquinolinone derivative.

Analysis of the quantum yields for the PET reaction led us to conclude that the overall reaction efficiency is mainly determined by the stability of an initially-formed ion radical pair intermediate, that is, by the relative rate of back ET in this intermediate.[10] In order to extend the synthetic utility of ET-initiated photocyclization reactions described above and also to develop pharmacologically active heterocyclic compounds having a structure related to papaverine,[11] we synthesized various (*Z*)-*N*-acyl-α-dehydro(methoxy-substituted phenyl)alaninamide derivatives [(*Z*)-**1a**–**k**] and investigated the effects of substituent and tertiary amine base as an electron donor on the selectivity of each **1**-derived photoproduct.

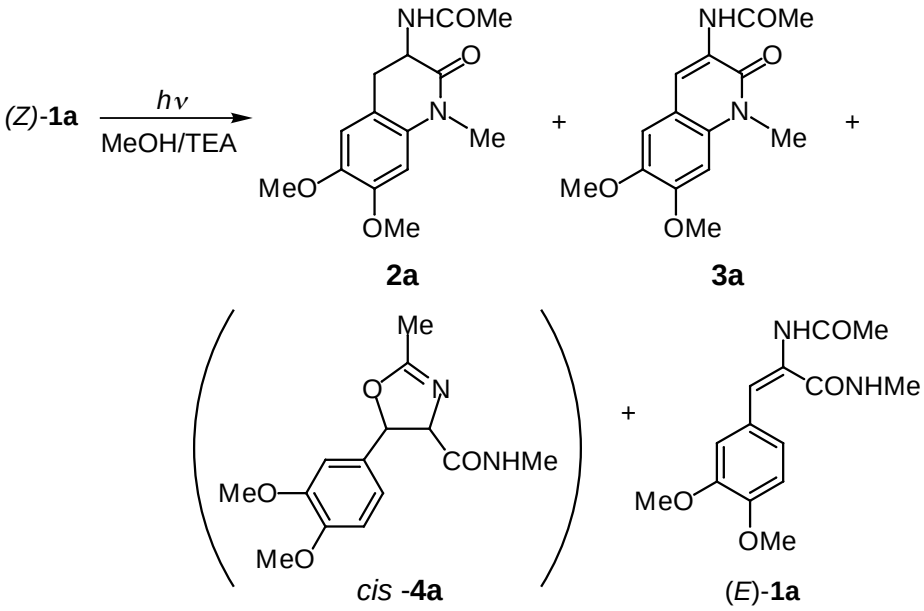


(*Z*)-**1a**: R= Me
(*Z*)-**1b**: R= *i*-Pr
(*Z*)-**1c**: R= *t*-Bu
(*Z*)-**1d**: R= CH_2Ph
(*Z*)-**1e**: R= $CH_2C_6H_4F$-4
(*Z*)-**1f**: R= $CH_2C_6H_4Cl$-4
(*Z*)-**1g**: R= $CH_2C_6H_3Cl_2$-3,4
(*Z*)-**1h**: R= $CH_2C_6H_3(OMe)_2$-3,4
(*Z*)-**1i**: R= $C_6H_3(OMe)_2$-2,4



(*Z*)-**1j**: R= Ph
(*Z*)-**1k**: R= $C_6H_3(OMe)_2$-2,4

The starting (*Z*)-isomers (**1a**–**k**) were prepared by the ring-opening reactions of the corresponding oxazolones with methylamine in excellent yields.[12] After a nitrogen-saturated methanol solution of (*Z*)-**1a** (3.75×10^{-3} mol dm^{-3}, 200 mL) containing triethylamine (TEA, 0.10 mol dm^{-3}) was irradiated with Pyrex-filtered light (>280 nm) from a 400 W high-pressure Hg lamp for 10 h at room temperature. Preparative thin-layer chromatography (silica gel) of the residual solid (that was obtained by evaporating the reaction mixture to dryness) allowed us to isolate 3-acetylamino-3,4-dihydro-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (**2a**, 17% isolated yield) and 3-acetylamino-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (**3a**, 5%) in addition to (*E*)-**1a** (25%). Careful ^{1}H NMR spectral analysis of the product mixture suggested that



Scheme 1

there is very little formation of 5-(3,4-dimethoxyphenyl)-2-methyl-4-methylaminocarbonyl-4,5-

dihydrooxazole (**4a**). Because the ring-proton signals of this product have larger $J_{4,5}$ value (10.4 Hz) as compared to those ($J_{4,5}$= 6–7 Hz) of the *trans*-isomer,[8,10] **4a** must be the *cis*-isomer (Scheme 1). Attempts to isolate this oxazole derivative from the mixture were unsuccessful owing to its poor yield. The findings that the photoproducts (**2a**–**4a**) are highly stable under the irradiation conditions used and that the area of ^{1}H NMR signals for unknown products is much smaller than that for these photoproducts allowed us to monitor the reaction by means of ^{1}H NMR spectroscopy in a fair accuracy, as shown in Table 1. The results in Table 1 demonstrate the rapid production of (*E*)-**1a** and the subsequent increase in compositions for **2a**–**4a** with the decrease of the isomer compositions. In addition to the structure of **2a**–**4a**, this observation strongly suggests that the excited-state (*E*)-isomer serves as a precursor of these products. In previous studies we found that the ET-initiated photocyclization of (*Z*)-*N*-acyl-α-dehydronaphthylalaninamides gives the corresponding 3,4-dihydrobenzo[*f*]quinolinone derivatives in high selectivities (along with minute amounts of 4,5-dihydrooxazoles) *via* an anion radical intermediate formed by ET from TEA to the singlet excited-state (*E*)-isomer.[6,10] On the other hand, the irradiation of a methanol solution of (*Z*)-*N*-acyl-α-dehydro(3-methoxyphenyl)alaninamides containing no TEA was found to afford regioselectively the corresponding 6-methoxy-2-quinolinone derivatives as major products.[7] Thus, these findings reveal that **2a** and **4a** are the products derived from the PET reaction of **1a** which takes place in competition with its photocyclization giving eventually **3a**.

Table 1. Relation between irradiation time and composition (%) of each compound obtained by the irradiation of (*Z*)-**1a** in methanol containing TEA (0.10 mol dm^{-3}) at room temperature

Compound	Irradiation time (h)				
	0	0.5	3	5	10
(Z)-**1a**	100	54	40	39	36
(E)-**1a**	0	42	42	39	34
2a	0	4	13	15	21
3a	0	0	4	6	7
cis-**4a**	0	0	1	1	2

Taking into account the idea that one simple method to discriminate between these two cyclization pathways is to employ tertiary amine of a different electron-donating ability, we chose TEA (pK_a= 10.6,[13] 10.8[14]), *N*,*N*-diisopropylethylamine (DPA, pK_a= 11.0[13]), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, pK_a= 12.8[13]) and examined the effects of these amines on the photoreactivity of **1a** and the selectivity for **2a**–**4a**. As clearly seen from the results shown in Table 2, the selectivity for **2a** is increased with increasing the electron-donating ability of the amine while the reverse is found for the selectivity for **3a**, though the oxazole derivative (**4a**) shows a similar selectivity irrespective of the amine examined. In addition to this product selectivity-amine basicity relationship, the finding that the photoreactivity is also enhanced as the

amine basicity is increased substantiates the above suggestion as well as the participation of an ion radical pair intermediate in the PET reaction of (*Z*)-**1**, therefore, leading us to propose Scheme 2. As already

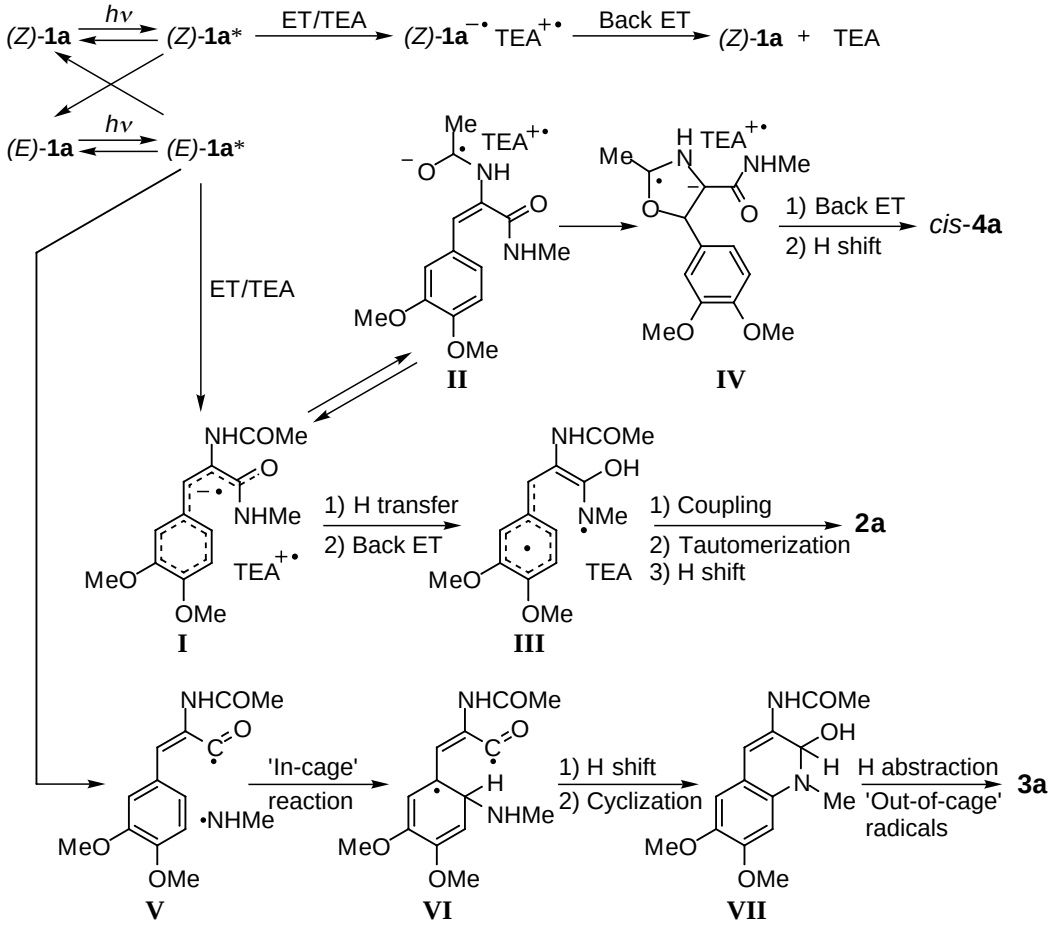
Table 2. Effects of amine basicity on the conversion of **1a** and the selectivity of **2a**–**4a**[a]

Amine	Conversion[b] (%)	Selectivity (%)[c]		
		2a	**3a**	**4a**
TEA	45	61	29	10
DPA	52	76	15	9
DBU	66	92	0	8

Table 3. Effects of DBU concentration on the conversion of **1a** and the selectivity of **2a**–**4a**[a]

DBU (mmol dm^{-3})	Conversion[b] (%)	Selectivity (%)[c]		
		2a	**3a**	**4a**
1	45	48	44	8
3	59	80	13	7
10	71	92	0	8

[a] Nitrogen-saturated methanol solutions of (*Z*)-**1a** (3.75×10^{-3} mol dm^{-3}, 10 mL) containing a given tertiary amine (0.10 mol dm^{-3} in Table 2) were placed in Pyrex tubes and sealed. Deaerated solutions were irradiated in parallel for 3 h at room temperature on a merry-go-round apparatus with Pyrex-filtered light from a 400 W high-pressure Hg lamp.
[b] Conversion was estimated by the sum of composition for **2a**, **3a**, and *cis*-**4a**.
[c] Selectivity was evaluated by dividing the composition for each product by the sum of composition for **2a**, **3a**, and *cis*-**4a**.



Scheme 2

discussed in the previous paper,[10] ET from TEA to the singlet excited-state (*E*)-**1a** forms the ion radical pair

intermediate (**I**) which may be in equilibrium with the ion radical pair intermediate (**II**). Hydrogen transfer from the amide nitrogen to the amide carbonyl oxygen in the intermediate (**I**) and the subsequent back ET to TEA cation radical affords TEA and the enol-type biradical (**III**), the coupling and tautomerization of which eventually generate dihydroquinolinone derivative (**2a**) *via* hydrogen shift. In competition with this cyclization process, the nucleophilic attack of the *N*-acetyl carbonyl oxygen anion upon the olefinic carbon takes place in **II** to give the cyclized anion radical (**IV**). Back ET to the TEA cation radical followed by hydrogen shift affords *cis*-**4a** preferentially.[8] The observation that the selectivity for **4a** is not strongly dependent on the basicity of the tertiary amine used suggests that the hydrogen-bonding solvation ability of this amine affects the relative stability of **I** being equilibrium with the intermediate (**II**), through which **4a** is formed. On the other hand, an efficient intramolecular ET in the excited-state (*E*)-isomer is a driving force for inducing the homolytic C(=O)–NHMe bond cleavage (owing to the so-called "*meta* effect"[15]) that gives the radical pair (**V**).[7] The 'in-cage' reaction of this radical pair produces the biradical (**VI**) while quinolinone derivative (**3a**) is obtained by hydrogen abstraction from the acetal (**VII**) by 'out-of-cage' radicals. Because the (*Z*)-**1a***-derived photoproducts such as isoquinoline derivative could not be detected in the reaction mixture, the ion radical pair, (*Z*)-**1a**$^{-\bullet}$ TEA$^{+\bullet}$, is considered to undergo exclusive back ET to regenerate (*Z*)-**1a** and TEA (Scheme 2).[6]

As already described, the fact that the photoproducts (**2a**–**4a**) are highly stable under the irradiation conditions makes it possible to estimate the product composition even at greater than 99% conversions of the starting α-dehydroarylalaninamides (**1**) and to discuss substituent effects on the selectivities of these products as well as the synthetic utility of the ET-initiated photocyclization of (*Z*)-**1**. Because it is preferable to minimize the concentration of DBU having a much higher boiling point than that of TEA,[16] the effects of DBU concentration on the conversion (photoreactivity) of **1a** and the product selectivity were explored in nitrogen-saturated methanol (Table 3). The data in Table 3 clearly show that both the conversion of **1a** and the selectivity of dihydroquinolinone derivative (**2a**) are increased with increasing the DBU concentration and also this selectivity reaches a nearly constant value at [DBU]= 0.010 mol dm^{-3}. In addition, the dependence of selectivity for **2a**–**4a** on the DBU concentration is very similar to that of this selectivity on the basicity of the tertiary amine summarized in Table 2. Hence this finding justifies the assumption that the hydrogen-bonding solvation of ion radical pair intermediates (**I** and **II**) by the amine is one of the key factors that control the relative stability of these intermediates.

In Table 4 are collected selectivities of the photoproducts (**2**–**4**) and isolated yields of 3,4-dihydro-2(1*H*)-quinolinones (**2a**–**k**). From any starting *N*-acyl-α-dehydroarylalaninamides we were able to obtain the desired dihydroquinolinones in high selectivities (71–94%) and also in good isolated yields (57–75%). Although small amounts of **3** and **4** remain in the reaction mixtures, these two products can be readily removed by recrystallization from ethanol. Additionally, analysis of *N*-acyl substituent effects on the product selectivity revealed that the introduction of bulky aliphatic acyl groups such as *i*-PrCO, *t*-BuCO, and $ArCH_2CO$ enhances the selectivity for **3** to some extent while the selectivity for **4** is increased 3–5 times by the replacement of acetyl by aromatic acyl group. The former finding implies that the bulky acyl group exerts its steric effect on ET in the excited state to lower the relative rate of this ET, and the increased contribution of the ion radical pair intermediate (**II**) in a given reaction system is suggested by the latter

finding. No formation of expected isoquinoline derivatives in any systems may be due to the exclusive progress of back ET in the ion radical pair, (*Z*)-**1**$^{-\bullet}$ DBU$^{+\bullet}$, as already described for (*Z*)-**1a**.

Table 4. Substituent effects on the selectivity for each product obtained by the 5h irradiation of *(Z)*-**1** (3.75×10^{-3} mol dm^{-3}) in methanol containing DBU (10 mmol dm^{-3}) at room temperature[a]

Compound	Selectivity (%)			Isolated yield of **2** (%)
	2	**3**	**4**[b]	
1a	94	0	6	75
1b	86	5	9	67
1c	82	6	12	74
1d	87	4	9	71
1e	89	4	7	69
1f	91	3	6	62
1g	88	5	7	63
1h	88	4	8	71
1i	82	0	18	69
1j	71	0	29	57
1k	82	0	18	67

[a] The conversion of **1** was nearly 100%.
[b] The sum of selectivity for *cis*- and *trans*-isomers.

In conclusion, the intermolecular PET reaction of *N*-acyl-α-dehydro(methoxy-substituted phenyl)alaninamides in methanol containing a small amount of DBU provides an efficient photochemical method for synthesizing 3,4-dihydro-2(1*H*)-quinolinone derivatives containing various substituents in high yields.

EXPERIMENTAL

General methods

^{1}H and ^{13}C NMR and IR spectra were taken with a JEOL JNM-ECA600 spectrometer and a Shimadzu IRPrestige-21 infrared spectrophotometer, respectively. Chemical shifts were determined using tetramethylsilane as an internal standard. UV absorption spectra were recorded on a Hitachi U-3300 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer PE2400 series II CHNS/O analyzer. TEA, DPA, and DBU were fractionally distilled from sodium hydroxide. Methanol was purified according to the standard procedure and freshly distilled prior to use.[16] All other reagents used were obtained from commercial sources and of the highest grade available.

General procedure for the synthesis of (*Z*)-2-alkyl-4-(methoxy-substituted benzylidene)-5(4*H*)-oxazolones and (*Z*)-2-aryl-4-(methoxy-substituted benzylidene)-5(4*H*)-oxazolones

N-Acylglycine (0.087 mol), methoxy-substituted benzaldehyde (0.090 mol), and sodium acetate (5.3 g, 0.067 mol) were added to acetic anhydride (50 mL) and the resulting mixtures were heated at 80–85 ℃ (*N*-acetylglycine), 70–80 ℃ for 1–2 h (*N*-aroylglycines), and 6–7 h (the other *N*-acylglycines) with stirring. The mixtures were cooled with ice and the solids separated out were collected by filtration with suction and washed with water, a small amount of cold ethanol and then with dry hexane. After the crude products had been air-dried at room temperature, these were recrystallized from hexane-chloroform to give yellow crystals (20–50%).

(*Z*)-4-(3,4-Dimethoxybenzylidene)-2-methyl-5(4*H*)-oxazolone: mp 161.0–162.0 ℃; IR (KBr): 1791, 1659, 1185 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 2.38 (3H, s), 3.80 (3H, s), 3.84 (3H, s), 7.09 (1H, d, *J*= 8.3 Hz), 7.16 (1H, s), 7.75 (1H, dd, *J*= 1.5, 8.3 Hz), 7.93 (1H, d, *J*= 1.5 Hz).

(*Z*)-4-(3,4-Dimethoxybenzylidene)-2-isopropyl-5(4*H*)-oxazolone: mp 84.0–85.0 ℃; IR (KBr): 1775, 1655, 1269 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.35 (6H, d, *J*= 6.9 Hz), 3.92 (1H, qq, *J*= 6.9, 6.9 Hz), 3.95 (6H, s), 6.91 (1H, d, *J*= 8.2 Hz), 7.11 (1H, s, H^e), 7.42 (1H, dd, *J*=1.4, 8.2 Hz), 8.19 (1H, d, *J*= 1.4 Hz).

(*Z*)-2-*tert*-Butyl-4-(3,4-dimethoxybenzylidene)-5(4*H*)-oxazolone: mp 135.0–136.0 ℃; IR (KBr): 1788, 1644, 1263 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.35 (9H, s), 3.95 (6H, s), 6.91 (1H, d, *J*= 8.2 Hz), 7.11 (1H, s), 7.45 (1H, dd, *J*= 8.2, 2.1 Hz), 8.11 (1H, d, *J*= 2.1 Hz).

(*Z*)-2-Benzyl-4-(3,4-dimethoxybenzylidene)-5(4*H*)-oxazolone: mp 152.0–153.0 ℃; IR (KBr): 1839, 1797, 1650, 1272 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.81 (3H, s), 3.93 (3H, s), 3.97 (2H, s), 6.88 (1H, d, *J*= 8.6 Hz), 7.11(1H, s), 7.27–7.39 (5H, m), 7.40 (1H, dd, *J*= 2.0, 8.6 Hz), 8.01 (1H, d, *J*= 2.0 Hz).

(*Z*)-4-(3,4-Dimethoxybenzylidene)-2-(4-fluorobenzyl)-5(4*H*)-oxazolone: mp 134.0–135.0 ℃; IR (KBr): 1774, 1653, 1018 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.83 (3H, s), 3.94 (3H, s), 3.95 (2H, s), 6.89 (1H, d, *J*= 8.3 Hz), 7.04 (2H, dd, *J*= 8.3, 8.9 Hz), 7.11 (1H, s), 7.34 (2H, dd, *J*= 5.5, 8.3 Hz), 7.42 (1H, dd, *J*= 2.1, 8.3 Hz), 7.98 (1H, d, *J*= 2.1 Hz).

(*Z*)-2-(4-Chlorobenzyl)-4-(3,4-dimethoxybenzylidene)-5(4*H*)-oxazolone: mp 145.5–146.0 ℃; IR (KBr): 1800, 1650, 1023 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.82 (3H, s), 3.94 (3H, s), 3.94 (2H, s), 6.89 (1H, d, *J*= 8.6 Hz), 7.11 (1H, s), 7.31 (2H, d, *J*= 8.6 Hz), 7.33 (2H, d, *J*= 8.6 Hz), 7.41 (1H, d, *J*= 8.6 Hz), 7.97 (1H, s).

(*Z*)-2-(3,4-Dichlorobenzyl)-4-(3,4-dimethoxybenzylidene)-5(4*H*)-oxazolone: mp 132.5–133.5 ℃; IR (KBr): 1786, 1651, 1024 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.84 (3H, s), 3.94 (2H, s), 3.94 (3H, s), 6.90 (1H, d, *J*= 8.2 Hz), 7.14 (1H, s), 7.22 (1H, dd, *J*= 2.1, 8.2 Hz), 7.41 (1H, dd, *J*= 1.4, 8.2 Hz), 7.44 (1H, d, *J*= 8.2 Hz), 7.50 (1H, d, *J*= 2.1 Hz), 7.96 (1H, d, *J*= 1.4 Hz).

(*Z*)-2-(3,4-Dimethoxybenzyl)-4-(3,4-dimethoxybenzylidene)-5(4*H*)-oxazolone: mp 157.0–158.0 ℃; IR (KBr): 1794, 1650, 1266 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.85 (3H, s), 3.87 (3H, s), 3.89 (3H, s), 3.91 (2H, s), 3.93 (3H, s), 6.84 (1H, d, *J*= 8.3 Hz), 6.88 (1H, d, *J*= 2.0 Hz), 6.89 (1H, d, *J*= 8.3 Hz), 6.92 (1H, dd, *J*= 2.0, 8.3 Hz), 7.10 (1H, s), 7.46 (1H, dd, *J*= 2.0, 8.3 Hz), 7.97 (1H, d, *J*= 2.0 Hz).

(*Z*)-4-(3,4-Dimethoxybenzylidene)-2-(2,4-dimethoxyphenyl)-5(4*H*)-oxazolone: mp 181.5–182.0 ℃; IR (KBr): 1773, 1601, 1277 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.90 (3H, s), 3.96 (6H, s), 4.04 (3H, s), 6.56 (1H, d, *J*= 2.3 Hz), 6.61 (1H, dd, *J*= 2.3, 8.6 Hz), 6.92 (1H, d, *J*= 8.3 Hz), 7.13 (1H, s), 7.49 (1H, d, *J*= 8.3 Hz), 8.02 (1H, d, *J*= 8.6 Hz), 8.24 (1H, s).

(*Z*)-4-(3-Methoxybenzylidene)-2-phenyl-5(4*H*)-oxazolone: mp 103.5–104.0 ℃; IR (KBr): 1800, 1659, 1200 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 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-(2,4-Dimethoxyphenyl)-4-(3-methoxybenzylidene)-5(4*H*)-oxazolone: mp 142.0–144.0 ℃; IR (KBr): 1776, 1650, 1296 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 3.90 (3H, s), 3.91 (3H, s), 3.98 (3H, s), 6.56 (1H, d, *J*= 2.0 Hz), 6.62 (1H, dd, *J*= 2.0, 9.0 Hz), 6.99 (1H, dd, *J*= 2.0, 7.8 Hz), 7.14 (1H, s), 7.35 (1H, dd, *J*= 7.8, 7.8 Hz), 7.62 (1H, d, *J*= 7.8 Hz), 7.99 (1H, d, *J*= 2.0 Hz), 8.04 (1H, d, *J*= 9.0 Hz).

General procedure for the synthesis of (*Z*)-*N*-acyl-α-dehydro(methoxy-substituted phenyl)alaninamide derivatives [(*Z*)-1a–k]

(*Z*)-2-Alkyl-4-(methoxy-substituted benzylidene)-5(4*H*)-oxazolone (for **1a**–**h**) or (*Z*)-2-aryl-4-(methoxy-substituted benzylidene)-5(4*H*)-oxazolone (for **1i**–**k**, 0.020 mol) was added to dry chloroform (200 mL) containing methylamine (40 wt% aqueous solution 1.6 g, 0.021 mol) and the resulting solution was allowed to stand for 1.0 h with stirring in an ice bath. The reaction mixture was concentrated to dryness and the resulting residue was dissolved in ethanol and then treated with activated charcoal powder. After removal of the solvent under reduced pressure, the crystalline solid obtained was recrystallized from ethanol-hexane affording colorless crystals (50–85%).

(*Z*)-2-Acetylamino-3-(3,4-dimethoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1a]: mp 205.0–205.5 ℃; IR (KBr): 3303, 1648, 1620 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.02 (3H, s), 2.66

(3H, d, *J*= 4.8 Hz), 3.76 (3H, s), 3.77 (3H, s), 6.97 (1H, d, *J*= 8.9 Hz), 7.08 (1H, s), 7.09 (1H, dd, *J*= 1.4, 8.9 Hz), 7.23 (1H, d, *J*= 1.4 Hz), 7.87 (1H, q, *J*= 4.8 Hz), 9.35 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 22.9, 26.2, 55.3, 55.5, 111.5, 112.3, 123.2, 126.8, 127.8, 128.3, 148.3, 149.3, 165.4, 169.3; *Anal*. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.04; H, 6.39; N, 9.78.

(*Z*)-3-(3,4-Dimethoxyphenyl)-2-isobutyrylamino-*N*-methyl-2-propenamide [(*Z*)-1b]: mp 205.0–205.5 ℃; IR (KBr): 3300, 1651, 1647 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.07 (6H, d, *J*= 5.9 Hz), 2.65 (3H, d, *J*= 4.8 Hz), 2.65 (1H, qq, *J*= 11.0, 5.9 Hz), 3.74 (3H, s), 3.74 (3H, s), 6.93 (1H, s), 6.95 (1H, d, *J*= 8.2 Hz), 7.09 (1H, dd, *J*= 8.2, 2.1 Hz), 7.18 (1H, d, *J*= 2.1 Hz), 7.73 (1H, q, *J*= 4.8 Hz), 9.24 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 19.2 (2C), 26.2, 33.7, 55.5 (2C), 112.9, 114.5, 122.9, 126.9, 127.3, 128.5, 148.3, 149.2, 165.8, 175.7; *Anal.* Calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.61; H, 6.85; N, 8.97.

(*Z*)-3-(3,4-Dimethoxyphenyl)-*N*-methyl-2-pivaloylamino-2-propenamide [(*Z*)-1c]: mp 192.0–193.0 ℃; IR (KBr): 3296, 1679, 1624 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.20 (9H, s), 2.67 (3H, d, *J*= 4.8 Hz), 3.75 (6H, s), 6.92 (1H, s), 6.95 (1H, d, *J*= 8.9 Hz), 7.08 (1H, dd, *J*= 8.9, 2.1 Hz), 7.19 (1H, d, *J*= 2.1 Hz), 7.60 (1H, q, *J*= 4.8 Hz), 8.92 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.1, 27.1(3C), 38.4, 55.5(2C), 111.4, 112.9, 123.0, 127.1, 127.5, 129.1, 148.3, 149.1, 166.2, 177.1; *Anal.* Calcd for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74. Found: C, 63.58; H, 7.24; N, 8.86.

(*Z*)-3-(3,4-Dimethoxyphenyl)-*N*-methyl-2-phenylacetylamino-2-propenamide [(*Z*)-1d]: mp 182.5–183.0 ℃; IR (KBr): 3291, 1676, 1637 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.65 (3H, d, *J*= 4.5 Hz), 3.61 (3H, s), 3.64 (2H, s), 3.74 (3H, s), 6.76 (1H, d, *J*= 8.6 Hz), 6.99 (1H, dd, J= 8.6, 1.7 Hz), 6.99 (1H, s), 7.11 (1H, d, J= 1.7 H^z), 7.24-7.31 (5H, m), 7.88 (1H, q, J= 4.5 Hz), 9.54 (1H, s); 13C NMR (150 MHz, DMSO-d6): δ 26.2, 42.1, 55.3, 55.4, 111.3, 112.9, 122.8, 126.4, 126.6, 127.9, 128.0, 128.2 (2C), 129.3 (2C), 135.6, 148.3, 149.1, 165.5, 169.7; *Anal.* Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.49; H, 6.11; N, 7.85.

(*Z*)-3-(3,4-Dimethoxyphenyl)-2-(4-fluorophenylacetylamino)-*N*-methyl-2-propenamide [(*Z*)-1e]: mp 175.0–175.5 ℃; IR (KBr): 3298, 3126, 1660, 1653 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.67 (3H, d, *J*= 4.8 Hz), 3.64 (2H, s), 3.64 (3H, s), 3.75 (3H, s), 6.79 (1H, d, *J*= 8.2 Hz), 6.97 (1H, dd, *J*= 8.2, 2.0 Hz), 7.02 (1H, s), 7.11 (1H, d, *J*= 2.0 Hz), 7.14 (2H, dd, *J*= 8.3, 8.9 Hz), 7.33 (2H, dd, *J*= 8.3, 5.5 Hz), 7.91 (1H, q, *J*= 4.8 Hz), 9.54 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.2, 41.2, 55.3, 55.4, 111.3, 112.9, 114.9 (2C, d, *J*=22 Hz), 122.8 (2C), 126.6, 127.9, 128.1, 131.8 (2C, d *J*= 3Hz), 148.3, 149.2, 161.1(1C, d, *J*= 241 Hz), 165.6, 169.7; *Anal.* Calcd for $C_{20}H_{21}N_2O_4F$: C, 64.51; H, 5.68; N, 7.52. Found: C, 64.25; H, 5.52; N, 7.38.

(*Z*)-2-(4-Chlorophenylacetylamino)-3-(3,4-dimethoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1f]: mp 180.0–180.5 ℃; IR (KBr): 3305, 3131, 1673, 1643 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6):

δ 2.66 (3H, d, *J*= 4.8 Hz), 3.63 (2H, s), 3.64 (3H, s), 3.74 (3H, s), 6.76 (1H, d, *J*= 8.2 Hz), 6.92 (1H, dd, *J*= 8.2, 1.8 Hz), 7.01 (1H, s), 7.10 (1H, d, *J*= 1.8 Hz), 7.33 (2H, d, *J*= 8.2 Hz), 7.38 (2H, d, *J*= 8.2 Hz), 7.91 (1H, q, *J*= 4.8 Hz), 9.54 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.2, 41.4, 55.3, 55.4, 111.3, 113.0, 122.7, 126.6, 127.8, 128.1 (3C), 131.2 (3C), 134.6, 148.2, 148.2, 165.4, 169.4; *Anal.* Calcd for $C_{20}H_{21}N_2O_4Cl$: C, 61.78; H, 5.44; N, 7.20. Found: C, 61.59; H, 5.15; N, 6.96.

(*Z*)-2-(3,4-Dichlorophenylacetylamino)-3-(3,4-dimethoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1g]: mp 173.5–174.0 ℃; IR (KBr): 3308, 2977, 1652, 1646 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.67 (3H, d, *J*= 4.8 Hz), 3.66 (2H, s), 3.66 (3H, s), 3.75 (3H, s), 6.76 (1H, d, *J*= 8.3 Hz), 6.94 (1H, dd, *J*= 1.4, 8.3 Hz), 7.03 (1H, s), 7.09 (1H, d, *J*= 1.4 Hz), 7.30 (1H, dd, *J*= 1.4, 8.2 Hz), 7.57 (1H, d, *J*= 1.4 Hz), 7.59 (1H, d, *J*= 8.2 Hz), 7.94 (1H, q, *J*= 4.8 Hz), 9.56 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.2, 41.0, 55.3, 55.4, 111.2, 113.1, 122.6, 126.6, 127.7, 128.4, 129.2, 128.9, 130.3, 130.7, 131.4, 136.8, 148.3, 149.2, 165.4, 169.0; *Anal.* Calcd for $C_{20}H_{20}N_2O_4Cl_2$: C, 56.75; H, 4.76; N, 6.62. Found: C, 56.50; H, 4.47; N, 6.75.

(*Z*)-3-(3,4-Dimethoxyphenyl)-2-(3,4-dimethoxyphenylacetylamino)-*N*-methyl-2-propenamide [(*Z*)-1h]: mp 180.5–181.0 ℃; IR (KBr): 3275, 2964, 1640, 1621 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.66 (3H, d, *J*= 4.8 Hz), 3.56 (2H, s), 3.63 (3H, s), 3.71 (3H, s), 3.74 (3H, s), 3.74 (3H, s), 6.73 (1H, d, *J*= 8.3 Hz), 6.83 (1H, dd, *J*= 1.7, 8.3 Hz), 6.91 (1H, d, *J*= 8.3 Hz), 6.92 (1H, dd, *J*= 2.0, 8.3 Hz), 6.93 (1H, d, *J*= 1.7 Hz), 7.01 (1H, s), 7.11 (1H, d, *J*= 2.0 Hz), 7.87 (1H, q, *J*= 4.8 Hz), 9.45 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.2, 41.9, 55.3 (2C), 55.4, 55.6, 111.0, 111.7, 113.0, 113.2, 121.3, 122.7, 126.7, 128.0 (3C), 147.6, 148.2, 148.5, 149.1, 165.6, 170.0; *Anal.* Calcd for $C_{22}H_{26}N_2O_6$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.47; H, 6.09; N, 6.96.

(*Z*)-2-(2,4-Dimethoxybenzoylamino)-3-(3,4-dimethoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1i]: mp 184.0–184.5 ℃; IR (KBr): 3350, 3332, 1632, 1620 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.68 (3H, d, *J*= 4.6 Hz), 3.57 (3H, s), 3.76 (3H, s), 3.85 (3H, s), 3.93 (3H, s), 6.68 (1H, dd, *J*= 2.3, 9.2 Hz), 6.72 (1H, d, *J*= 2.3 Hz), 6.96 (1H, d, *J*= 8.6 Hz), 7.05 (1H, s), 7.15 (1H, d, *J*= 8.6 Hz), 7.22 (1H, s), 7.86 (1H, d, *J*= 9.2 Hz), 7.89 (1H, d, *J*= 4.6 Hz), 9.38 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 26.3, 55.0, 55.4, 55.6, 56.2, 98.5, 105.9, 111.5, 112.2, 114.2, 123.0, 126.9, 127.1, 128.1, 132.8, 148.3, 149.2, 158.9, 163.4, 163.5, 165.6; *Anal.* Calcd for $C_{21}H_{24}N_2O_6$: C, 62.99; H, 6.04; N, 7.00. Found: C, 62.83; H, 6.17; N, 6.86.

(*Z*)-2-Benzoylamino-3-(3-methoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1j]: mp 181.5–182.5 ℃; IR (KBr): 3244, 1635 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ 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 (150 MHz, DMSO-d_6): δ 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, 9.03.

(*Z*)-2-(2,4-Dimethoxybenzoylamino)-3-(3-methoxyphenyl)-*N*-methyl-2-propenamide [(*Z*)-1k]: mp 150.5–151.5 ℃; IR (KBr): 3308, 3300, 1650, 1632 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.69 (3H, d, *J*= 4.9 Hz), 3.67 (3H, s), 3.85 (3H, s), 3.90 (3H, s), 6.68 (1H, dd, *J*= 2.5, 7.9 Hz), 6.72 (1H, d, *J*= 2.5 Hz), 6.90 (1H, dd, *J*= 1.8, 8.6 Hz), 6.93 (1H, s), 7.14 (1H, d, *J*= 1.8 Hz), 7.16 (1H, d, *J*= 7.9 Hz), 7.30 (1H, dd, *J*= 7.9, 8.6 Hz), 7.84 (1H, d, *J*= 7.9 Hz), 7.98 (1H, q, *J*= 4.9 Hz), 9.49 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 54.9, 55.6, 56.1 (2C), 98.5, 106.0, 114.1, 114.2 (2C), 121.7, 125.2, 129.6, 130.8, 132.8, 135.6, 158.9, 159.2, 163.3, 163.5, 165.5; *Anal*. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.76; H, 6.01; N, 7.74.

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

In order to examine the irradiation time dependence of the product distribution and composition, a methanol solution of (*Z*)-**1** (3.75×10^{-3} mol dm^{-3}, 200 mL) containing TEA (0.10 mol dm^{-3}), placed in a Pyrex vessel, was irradiated under nitrogen at rt with Pyrex-filtered light from a 400 W high-pressure Hg lamp (internal 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 ^1H NMR spectral analysis. The composition was estimated from the area ratio of a given ^1H NMR signal for each compound. The remaining solution containing TEA was concentrated to dryness in vacuo and the resulting residue was subjected to preparative thin layer chromatography over silica gel. The mixed solvents of chloroform and ethyl acetate were used as developing solvents.

On the other hand, a nitrogen-saturated methanol solution of (*Z*)-**1** (3.75×10^{-3} mol dm^{-3}, 500 mL) containing DBU (0.010 mol dm^{-3}), placed in a Pyrex vessel, was irradiated for 5 h with Pyrex-filtered light from a 400 W high-pressure Hg lamp at room temperature. After 5 h irradiation, an appropriate amount of the solution (5 mL) being irradiated was pipetted off and concentrated to dryness in vacuo giving the residue which was subjected to ^1H NMR spectral analysis in DMSO-d_6. The remaining solution was concentrated to dryness under reduced pressure and the resulting residue was subjected to column chromatography over silica gel (230 mesh, Merck) eluting with chloroform-ethyl acetate. For the purpose of isolating the photoproducts, preparative TLC plate (silica gel) was also used. Physical and spectroscopic data of purified 3,4-dihydroquinolinones (**2a**–**k**), quinolinone (**3a**), and (*E*)-**1a** are as follows. Attempts to isolate other quinolinones and (*E*)-isomers were not made.

3-Acetylamino-3,4-dihydro-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (2a): mp 165.0–166.0 ℃ (EtOH); IR (KBr): 3318, 1679, 1636 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 1.91(3H, s), 2.76 (1H, dd, *J*= 6.2, 15.1 Hz), 2.91 (1H, dd, *J*= 14.5, 15.1 Hz), 3.29 (3H, s), 3.74 (3H, s), 3.80 (3H, s), 4.38 (1H, ddd, *J*= 6.2, 8.3, 14.5 Hz), 6.74 (1H, s), 6.90 (1H, s), 8.18 (1H, d, *J*= 8.3 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 22.6, 30.0, 30.8, 48.5, 55.6, 55.9, 101.4, 112.4, 115.6, 132.9, 144.3, 148.0, 167.9, 169.2; *Anal*. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.38; H, 6.41; N, 9.97.

3,4-Dihydro-6,7-dimethoxy-3-isobutyrylamino-1-methyl-2(1*H*)-quinolinone (2b): mp 179.0–180.0 ℃ (EtOH); IR (KBr): 3334, 1691, 1638 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 1.03 (3H, d, *J*= 6.1 Hz), 1.05 (3H, d, *J*= 6.9 Hz), 2.49 (3H, qq, *J*= 6.1, 6.9 Hz), 2.79 (1H, dd, *J*= 6.2, 15.1 Hz), 2.87 (1H, dd, *J*= 14.5, 15.1 Hz), 3.29 (3H, s), 3.73 (3H, s), 3.80 (3H, s), 4.38 (1H, ddd, *J*= 6.2, 7.6, 14.5 Hz), 6.74 (1H, s), 6.91 (1H, s), 8.03 (1H, d, *J*= 7.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 19.5 (2C), 30.0, 30.7, 33.9, 48.2, 55.9 (2C), 101.4, 112.4, 115.7, 133.0, 144.3, 148.0, 168.0, 176.1; *Anal.* Calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.35; H, 7.11; N, 9.05.

3,4-Dihydro-6,7-dimethoxy-1-methyl-3-pivaloylamino-2(1*H*)-quinolinone (2c): mp 179.0–180.0 ℃ (EtOH); IR (KBr): 3325, 1676, 1639 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 1.15 (9H, s), 2.83 (1H, dd, *J*= 14.5, 15.1 Hz), 2.91 (1H, dd, *J*= 6.2, 15.1 Hz), 3.29 (3H, s), 3.73 (3H, s), 3.80 (3H, s), 4.38 (1H, ddd, *J*= 6.2, 7.6, 14.5 Hz), 6.74 (1H, s), 6.91 (1H, s), 7.60 (1H, d, *J*= 7.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 27.3 (3C), 30.0, 30.4, 38.0, 48.4, 55.9 (2C), 101.4, 112.4, 115.9, 133.0, 144.3, 148.0, 168.0, 176.1; *Anal.* Calcd for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74. Found: C, 63.46; H, 7.22; N, 8.61.

3,4-Dihydro-6,7-dimethoxy-1-methyl-3-phenylacetylamino-2(1*H*)-quinolinone (2d): mp 192.0–193.0 ℃ (EtOH); IR (KBr): 3288, 1677, 1628 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.75 (1H, dd, *J*= 6.2, 15.1 Hz), 2.86 (1H, dd, *J*= 14.4, 15.1 Hz), 3.52 (2H, s), 3.67 (3H, s), 3.74 (3H, s), 4.35 (1H, ddd, *J*= 6.2, 7.6, 14.4 Hz), 6.70 (1H, s), 6.86 (1H, s), 7.16–7.19 (1H, m), 7.24–7.26 (4H, m), 8.34 (1H, d, *J*= 7.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 30.7, 42.1, 48.6, 55.9, 56.0, 101.5, 112.5, 115.6, 126.3, 128.2 (2C), 129.0 (2C), 133.0, 136.3, 144.4, 148.1, 167.8, 170.1; *Anal.* Calcd for $C_{20}H_{22}N_2O_4$: C, 67.43; H, 6.28; N, 7.86. Found: C, 67.78; H, 6.26; N, 7.90.

3,4-Dihydro-6,7-dimethoxy-3-(4-fluorophenylacetylamino)-1-methyl-2(1*H*)-quinolinone (2e): mp 202.0–203.0 ℃ (EtOH); IR (KBr): 3352, 1684, 1640 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.78 (1H, dd, *J*= 6.2, 15.1 Hz), 2.91 (1H, dd, *J*= 14.4, 15.1 Hz), 3.31 (3H, s), 3.53 (2H, s), 3.71 (3H, s), 3.79 (3H, s), 4.38 (1H, ddd, *J*= 6.2, 7.5, 14.4 Hz), 6.74 (1H, s), 6.90 (1H, s), 7.13 (2H, dd, *J*= 8.9, 9.0 Hz), 7.33 (2H, dd, *J*= 6.2, 9.0 Hz), 8.34 (1H, d, *J*= 7.5 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 30.7, 48.6, 55.9, 56.0, 79.1, 101.5, 112.4, 114.8 (2C, d, *J*= 22 Hz), 115.6, 130.8 (2C, d, *J*= 7 Hz), 132.4, 133.0, 144.3, 148.1, 160.9 (1C, d, *J*= 241 Hz), 167.8, 170.0; *Anal.* Calcd for $C_{20}H_{21}N_2O_4F$: C, 64.51; H, 5.68; N, 7.52. Found: C, 64.25; H, 5.54; N, 7.31.

3-(4-Chlorophenylacetylamino)-3,4-dihydro-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (2f): mp 202.0–203.0 ℃ (EtOH); IR (KBr): 3346, 1681, 1643 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.77 (1H, dd, *J*= 6.1, 15.1 Hz), 2.91 (1H, dd, *J*= 14.4, 15.1 Hz), 3.29 (3H, s), 3.53 (2H, s), 3.71 (3H, s), 3.78 (3H, s), 4.38 (1H, ddd, *J*= 6.1, 8.3, 14.4 Hz), 6.73 (1H, s), 6.89 (1H, s), 7.31 (2H, d, *J*= 8.2 Hz), 7.35 (2H, d, *J*= 8.2 Hz), 8.43 (1H, d, *J*= 8.3 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 30.7, 41.3, 48.6, 55.9, 56.0, 101.5, 112.4, 115.6, 128.1 (2C), 130.9 (2C), 131.1, 133.0, 135.3, 144.3, 148.1,

167.7, 169.7; *Anal.* Calcd for $C_{20}H_{21}N_2O_4Cl$: C, 61.78; H, 5.44; N, 7.20. Found: C, 61.78; H, 5.30; N, 7.41.

3-(3,4-Dichlorophenylacetylamino)-3,4-dihydro-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (2g): mp 177.0–178.0 ℃ (EtOH); IR (KBr): 3325, 1683, 1635 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.79 (1H, dd, *J*= 6.1, 15.2 Hz), 2.92 (1H, dd, *J*= 14.4, 15.2 Hz), 3.30 (3H, s), 3.58 (2H, s), 3.72 (3H, s), 3.79 (3H, s), 4.37 (1H, ddd, *J*= 6.1, 8.2, 14.4 Hz), 6.75 (1H, s), 6.91 (1H, s), 7.30 (1H, dd *J*= 2.1, 8.2 Hz), 7.58 (1H, d, *J*= 8.2 Hz), 7.59 (1H, d, *J*= 2.1 Hz), 8.99 (1H, d, *J*= 8.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 30.6, 48.7, 55.9, 56.0, 101.5, 112.4, 115.6, 129.1, 129.5, 130.3, 130.7, 131.1 (2C), 137.4, 144.4, 148.1, 167.7, 169.3; *Anal.* Calcd for $C_{20}H_{20}N_2O_4Cl_2$: C, 56.75; H, 4.76; N, 6.62. Found: C, 56.50; H, 4.65; N, 6.44.

3,4-Dihydro-6,7-dimethoxy-3-(3,4-dimethoxyphenylacetylamino)-1-methyl-2(1*H*)-quinolinone (2h): mp 191.0–192.0 ℃ (EtOH); IR (KBr): 3290, 1642, 1618 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.75 (1H, dd, *J*= 6.2, 15.1 Hz), 2.90 (1H, dd, *J*= 14.4, 15.1 Hz), 4.37 (1H, ddd, *J*= 6.2, 7.6, 14.4 Hz), 6.73 (1H, s), 6.80 (1H, d, *J*= 7.6 Hz), 6.86 (1H, d, *J*= 7.6 Hz), 6.89 (1H, s), 6.95 (1H, s), 8.28 (1H, d, *J*= 7.6 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 30.7, 41.8, 48.6, 55.4, 55.5, 55.9, 56.0, 101.5, 111.8, 112.5, 112.9, 115.6, 121.0, 128.6, 133.0, 144.3, 147.5, 148.0, 148.5, 167.8, 170.3; *Anal*. Calcd for $C_{22}H_{26}N_2O_6$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.67; H, 5.99; N, 6.61.

3,4-Dihydro-6,7-dimethoxy-3-(2,4-dimethoxybenzoylamino)-1-methyl-2(1*H*)-quinolinone (2i): mp 203.5–205.0 ℃ (EtOH); IR (KBr): 3372, 1643, 1605 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.80 (1H, dd, *J*= 5.7, 14.9 Hz), 3.30 (1H, dd, *J*= 14.3, 14.9 Hz), 3.34 (3H, s), 3.76 (3H, s), 3.81 (3H, s), 3.84 (3H, s), 3.97 (3H, s), 4.49 (1H, ddd, *J*= 5.2, 5.7, 14.3 Hz), 6.68 (1H, dd, *J*= 2.3, 9.2 Hz), 6.71 (1H, d, *J*= 2.3 Hz), 6.80 (1H, s), 6.96 (1H, s), 7.94 (1H, d, *J*= 9.2 Hz), 8.81 (1H, d, *J*= 5.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.3, 30.7, 49.6, 55.6, 55.9, 56.0, 56.3, 98.7, 101.7, 106.0, 112.5, 113.7, 116.0, 132.7, 132.8, 144.5, 148.1, 159.0, 163.2, 163.8, 168.0; *Anal.* Calcd for $C_{21}H_{24}N_2O_6$: C, 62.67; H, 6.51; N, 6.96. Found: C, 62.46; H, 6.39; N, 6.84.

3-Benzoylamino-3,4-dihydro-6-methoxy-1-methyl-2(1*H*)-quinolinone (2j): mp 127.0–127.5 ℃ (EtOH); IR (KBr): 3279, 1676, 1630 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 3.01 (1H, dd, *J*= 5.5, 14.8 Hz), 3.14 (1H, dd, *J*= 14.4, 14.8 Hz), 3.29 (3H, s), 3.75 (3H, s), 4.68 (1H, ddd, *J*= 5.5, 8.2, 14.4 Hz), 6.88 (1H, dd, *J*= 2.7, 8.9 Hz), 6.92 (1H, d, *J*= 2.7 Hz), 7.08 (1H, d, *J*= 8.9 Hz), 7.51 (2H, dd, *J*= 6.9, 6.9 Hz), 7.57 (1H, dd, *J*= 6.9, 6.9 Hz), 7.90 (2H, d, *J*= 6.9 Hz), 8.70 (1H, d, *J*= 8.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.0, 31.2, 48.6, 55.3, 112.5, 113.9, 116.1, 125.7, 127.3 (2C), 128.3 (2C), 131.4, 133.1, 134.0, 154.9, 166.1, 167.7; *Anal.* Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.35; H, 5.88; N, 8.84.

3,4-Dihydro-3-(2,4-dimethoxybenzoylamino)-6-methoxy-1-methyl-2(1*H*)-quinolinone (2k): mp 160.5–161.5 ℃ (EtOH); IR (KBr): 3394, 1650, 1611 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 3.35 (1H, dd, *J*= 5.5, 15.1 Hz), 2.89 (1H, dd, *J*= 15.1, 14.4 Hz), 3.32 (3H, s), 3.76 (3H, s), 3.84 (3H, s), 3.97 (3H, s), 4.50 (1H, ddd, *J*= 5.5, 7.9, 14.4 Hz), 6.68 (1H, dd, *J*= 2.1, 8.9 Hz), 6.71 (1H, d, *J*= 2.8 Hz), 6.89 (1H, dd, *J*= 2.8, 8.9 Hz), 6.94 (1H, d, *J*= 2.1 Hz), 7.11 (1H, d, *J*= 8.9 Hz), 7.94 (1H, d, *J*= 8.9 Hz), 8.81 (1H, d, *J*= 7.9 Hz); ^{13}C NMR (150 MHz, DMSO-d_6): δ 30.1, 31.3, 49.3, 55.3, 55.5, 56.2, 98.7, 106.0, 112.6, 113.7, 113.9, 116.4, 125.9, 132.7, 133.0, 155.1, 159.0, 163.3, 163.9, 167.8; *Anal*. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.66; H, 5.81; N, 7.67.

3-Acetylamino-6,7-dimethoxy-1-methyl-2(1*H*)-quinolinone (3a): mp 195.0–196.0 ℃ (EtOAc); IR (KBr): 3377, 1688, 1636 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 2.17 (3H, s), 3.74 (3H, s), 3.81 (3H, s), 3.91 (3H, s), 6.99 (1H, s), 7.26 (1H, s), 8.59 (1H, s), 9.33 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 24.1, 30.2, 55.7, 55.8, 98.1, 109.5, 113.1, 120.4, 125.6, 130.6, 145.2, 150.2, 156.7, 169.3; *Anal*. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.88; H, 5.56; N, 9.86.

(*E*)-1a: mp 142.5–143.0 ℃ (EtOAc); IR (KBr): 3275, 1686, 1643, 1624 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ 1.93 (3H, s), 2.57 (3H, d, *J*= 4.8 Hz), 3.69 (3H, s), 3.73 (3H, s), 6.72 (1H, s), 6.75 (1H, dd, *J*= 2.1, 8.3 Hz), 6.86 (1H, d, *J*= 2.1 Hz), 6.97 (1H, d, *J*= 8.3 Hz), 7.97 (1H, d, *J*= 4.8 Hz), 9.50 (1H, s); ^{13}C NMR (150 MHz, DMSO-d_6): δ 23.3, 25.8, 55.3, 55.4, 111.2, 111.6, 115.4, 120.8, 127.9, 131.8, 147.8, 148.2, 165.5, 168.0; *Anal.* Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.40; H, 6.40; N, 9.97.

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