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Preferential formation of *cis*-4,5-dihydrooxazole derivatives via photoinduced electron transfer-initiated cyclization of *N*-acyl-α-dehydroarylalanine alkyl esters

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Abstract—The alkyl, aryl, and acyl substituent effects on the photoinduced electron transfer-initiated cyclization reaction of the title compounds (**1**) were investigated in polar solvents from mechanistic and synthetic points of view. The irradiation of (*Z*)-**1** in methanol containing triethylamine (TEA) was found to quantitatively give *cis*- and *trans*-4,5-dihydrooxazole derivatives (*cis*-**2** and *trans*-**2**). In addition to thermodynamic considerations for electron transfer and fluorescence quenching in the presence of TEA, acyl and aryl substituent effects on the emission intensity and photoreactivity of **1** confirmed the involvement of consecutive electron transfer reactions that form (*E*)-arylmethylene radical anion and (*E*)-*N*-acyl radical anion intermediates. It was also confirmed that the cyclization of the latter intermediate eventually leads to **2**. On the basis of the finding that the selectivity for *cis*-**2** is greatly increased with increasing the steric bulkiness of alkyl and aryl substituents in **1**, it was concluded that steric hindrance of these substituents toward hydrogen shift in the cyclized biradical intermediate, precursor of **2**, is responsible for the kinetically controlled hydrogen shift in this intermediate. A product composition analysis showed that the protic polar solvent, methanol, of hydrogen-bonding solvation ability is a most suitable solvent for the photocyclization reactions examined.

1. Introduction

Excited-state chemistry for organic compounds has continued to contribute to the development of new synthetic methods that enable the construction of various hetero atom-containing ring systems.[1] In recent years much attention is being devoted to studies regarding photoinduced electron transfer (PET) reactions, owing to the fact that many of these reactions initiated by an electron transfer (ET) give pharmaceutically useful heterocyclic compounds in high chemical and quantum yields.[1,2] In previous studies we found that *N*-acetyl-α-dehydrophenylalaninamides in polar solvents undergo a novel photocyclization giving isoquinoline and 1-azetine derivatives in satisfactory yields but with low efficiency.[3] The use of *N*-acetyl-α-dehydrophenylalanine alkyl esters as the starting α-dehydroamino acid derivatives enabled the selective formation of the corresponding isoquinolines by their photocyclization.[4] Interestingly, one-electron reduction of 1-naphthyl-substituted *N*-acetyl-α-dehydroalaninamides was found to proceed efficiently affording 3,4-dihydrobenzoquinolinone derivatives in high selectivity.[5] This finding demonstrates the synthetic utility of PET-initiated cyclization of *N*-acyl-α-dehydroamino acids. In these photocyclization reactions the corresponding isoquinoline and 4,5-dihydrooxazole derivatives were obtained as minor products. Replacement of acetyl by benzoyl as the *N*-acyl group resulted in an enhancement in selectivity for the dihydrobenzoquinolinone derivatives without any detectable formation of substituted isoquinolines, owing to large steric hindrance of the benzoyl group. In addition, the structural transformation of *N*-benzoyl-α-dehydroalaninamides into the corresponding alanine alkyl esters makes it impossible to generate the dihydrobenzoquinolinone derivatives through the PET-initiated cyclization. Accordingly, we were led to predict that *N*-aroyl-α-dehydronaphthylalanine alkyl esters in the excited singlet state undergo one-electron reduction in the presence of tertiary amine to selectively give the corresponding *cis*- and *trans*-4,5-dihydrooxazole derivatives. Because there is no photochemical synthetic route to dihydrooxazole derivatives though several routes to these derivatives are known,[6] the above prediction stimulated us to explore PET reactions of *N*-aroyl-α-dehydroarylalanine alkyl esters, hoping to

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develop an efficient and selective phototransformation method enabling the construction of a pharmaceutically important dihydrooxazole ring.[6h,7] To this end we designed and synthesized (*Z*)-*N*-(4-substituted benzoyl)- and (*Z*)-*N*-pivaloyl-α-dehydroarylalanine alkyl esters [(*Z*)-**1a–q**] (Chart 1) and examined substituent, solvent, and triethylamine (TEA) concentration effects on the photoreactivity of **1** and the product composition.

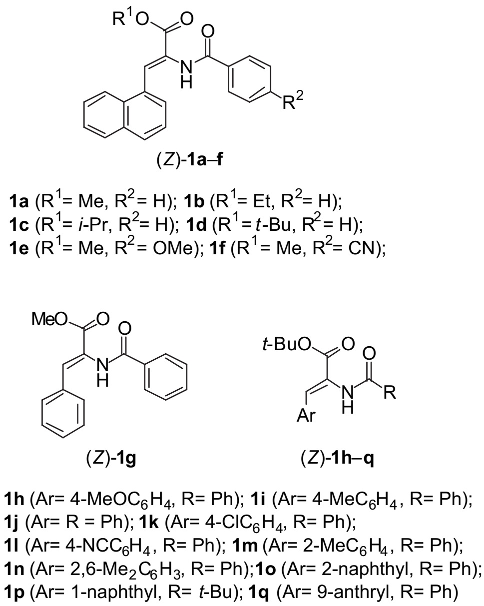
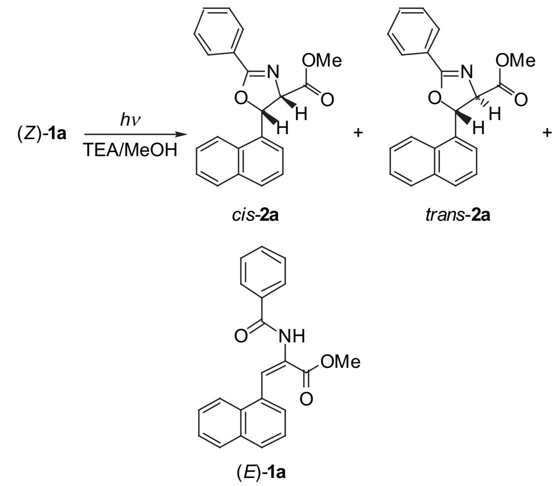


Chart 1.

2. Results and discussion

2.1. Product analysis and composition

The starting (*Z*)-isomers were prepared in reasonable yields (30–90%) by the ring-opening reactions of (*Z*)-2-aryl-4-(1-arylmethylene)-5(4*H*)-oxazolones with the corresponding alcohols in the presence of TEA.[4,8] After a nitrogen-saturated methanol solution of (*Z*)-**1a** (4.0×10^{-3} mol dm^{-3}, 500 mL) containing TEA (0.10 mol dm^{-3}) was irradiated with Pyrex-filtered light (>280 nm) from a 400 W high-pressure Hg lamp for 5 h at room temperature (conversion, 100%), the reaction mixture obtained was subjected to preparative thin layer chromatography over silica gel (eluent: EtOAc–hexane or EtOAc–$CHCl_3$). This chromatography allowed us to isolate *cis*- and *trans*-4-methoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazoles (*cis*-**2a**, 30%; *trans*-**2a**, 58% yield) having the vicinal coupling constants ($J_{4,5}$) of 10.3 and 6.9 Hz in DMSO-d_6, respectively, as shown in Scheme 1. The (*E*)-isomer of **1a** was isolated independently from the reaction mixture (40% yield), which was irradiated for 0.5 h under the same conditions (conversion, 16.5%), by similar workup (Scheme 1). The structure of the isolated products was determined based on their spectroscopic and physical properties. In addition, X-ray analysis of *cis*-**2a**- and *trans*-**2a**-derived single crystals provided definitive evidence for the structure of these two isomers (Fig. 1).[9] The irradiation of (*Z*)-**1b–p** in nitrogen-saturated methanol under the same conditions gave the corresponding *cis*- and *trans*-dihydrooxazole isomers in quantitative ^{1}H NMR yields at their >99% conversions but (*Z*)-**1q** underwent a secondary photodecomposition to give unknown products at relatively high conversions of this starting ester derivative (>50%).



Scheme 1.

2.2. Inter- and intramolecular electron transfer and kinetically controlled reactions

The finding that the photoproducts **2a–p** are stable enough such that they undergo only negligible decomposition under the irradiation conditions employed 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

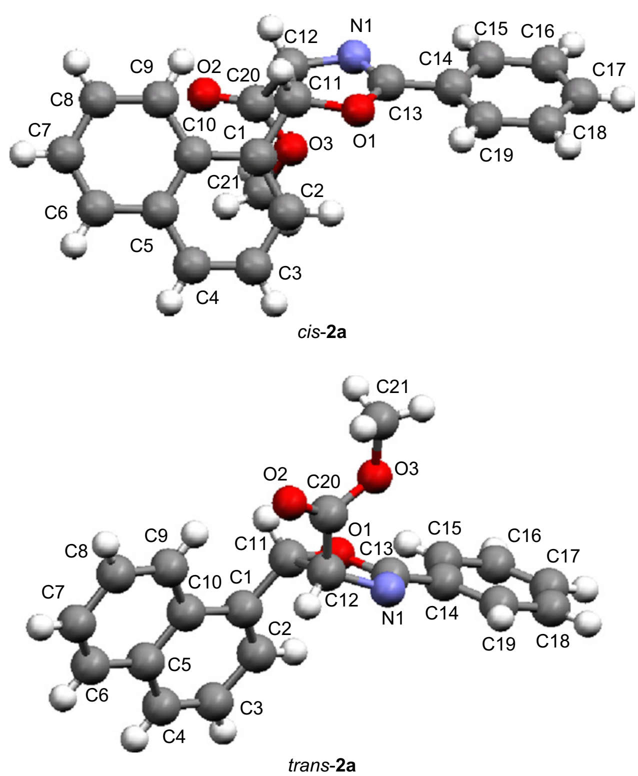


Figure 1. Crystal structures of *cis*-**2a** and *trans*-**2a**.

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

Irradiation time (h)	Composition (%)				*cis*-**2a**/*trans*-**2a**
	(*Z*)-**1a**	(*E*)-**1a**	*cis*-**2a**	*trans*-**2a**	
0	100	0	0	0	—
0.5	30.1	53.4	11.5	5.0	2.3
1	24.4	44.1	21.0	10.5	2.0
2	14.2	25.4	36.9	23.6	1.6
3	5.6	9.8	46.0	38.6	1.2
5	0	0	36.9	63.1	0.6

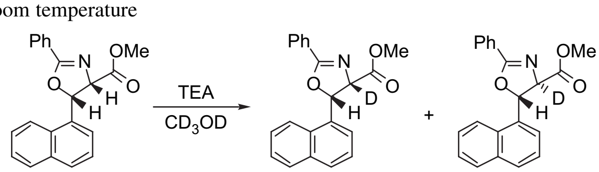
Table 3. Effects of TEA concentration on the conversion of **1a** and composition of each compound, obtained by the 3 h irradiation of (*Z*)-**1a** in MeOH at room temperature

TEA (mol dm^{-3})	Conversion (%)	Composition (%)				*cis*-**2a**/ *trans*-**2a**
		(*Z*)-**1a**	(*E*)-**1a**	*cis*-**2a**	*trans*-**2a**	
0	<0.1	>35.5	>65.4	<0.1	<0.1	—
0.01	48.7	17.8	33.5	38.8	9.9	3.9
0.05	70.4	10.2	19.5	48.2	22.2	2.2
0.10	74.6	8.8	16.6	43.9	30.7	1.4
0.20	80.2	7.0	12.8	36.4	43.8	0.8

subsequent increase in compositions for *cis*-**2a** and *trans*-**2a** with the decrease of (*E*)- and (*Z*)-isomer compositions, being consistent with the mechanism in which either of these isomers serves as a precursor of the products. Since the bond formed between the *N*-benzoyl carbonyl oxygen and the olefinic carbon in the naphthylmethylene moiety constructs a 4,5-dihydrooxazole ring, we suggest that the (*E*)-isomer serves as a precursor of **2**. Inspection of the data given in Table 1 also revealed that the composition ratio of *cis*-**2a** to *trans*-**2a** decreases with irradiation time. The finding that the heat of formation for *cis*-**2a** (ΔH_f= −232.8 kJ mol^{-1}) is greater than that (−237.0 kJ mol^{-1}) for *trans*-**2a** indicates the occurrence of TEA-catalyzed isomerization to the thermodynamically more stable trans-isomer.[10] This was substantiated by the observation that on allowing a deuterated methanol (CD_3OD) solution of *cis*-**2a** (4.0×10^{-3} mol dm^{-3}, 1.0 mL) containing TEA (0.10 mol dm^{-3}) to stand at room temperature, the isomerization to the trans-isomer slowly proceeds to furnish a 9:1 equilibrium mixture of *trans*-**2a** and *cis*-**2a**, respectively, after 7 days (Table 2). Additionally, a deuterium atom was incorporated at the 4-position on the oxazole ring when the equilibrium was established, confirming the existence of a carbanion intermediate in the isomerization process.

In order to examine the effect of TEA concentration on the photoreactivity of **1a** and the product compositions, nitrogen-saturated methanol solutions of (*Z*)-**1a** (4.0×10^{-3} mol dm^{-3}, 10 mL), containing varying amounts of TEA were irradiated in parallel for 3 h on a merry-go-round-type irradiation equipment using the same filter and light source. ^{1}H NMR spectral analysis of the reaction mixture obtained after usual workup gave the data collected in Table 3, which demonstrate that the reactivity is increased with an increase in TEA concentration while negligible amounts of the products are observed without TEA. This is consistent with the participation of a PET mechanism. The data of Table 3 also show that the composition ratio of *cis*-**2a** to *trans*-**2a** decreases with increasing TEA concentration, substantiating the occurrence of TEA-catalyzed isomerization to the trans-isomer, as already described above. Thus, we are able to preferentially obtain either of these two isomers by controlling the amine concentration and also to mainly generate the trans-isomer by allowing the reaction mixture to stand in the presence of a tertiary amine having high basicity. Because more evidence are required in support of the PET mechanism for the cyclization of *N*-acyl-α-dehydroarylalanine alkyl esters, we attempted to quench the fluorescence of (*Z*)-**1q** showing relatively strong emission by TEA and then to estimate free energy change (ΔG_{et}) in electron transfer from TEA to the singlet excited-state **1a**, the fluorescence of which was too weak to be detected. As clearly shown in Figure 2, fluorescence arising from the anthrylmethylene chromophore in **1q** was quenched by TEA according to the Stern–Volmer equation: I_0/I=1+1.57[TEA], where I and I_0 are the fluorescence intensities of **1q** with and without TEA, respectively. Because singlet–singlet energy transfer from the excited-state anthryl group to TEA is highly endothermic (UV spectral analysis), the above observation substantiates an ET emission quenching. Furthermore, the simplified Weller equation: ΔG_{et}/kJ mol^{-1}=96.5 $(E_{ox}-E_{red})-E_S$,[11] where E_{ox}, E_{red}, and E_S refer to the oxidation potential of TEA

Table 2. Relation between reaction time and composition (%) of each compound obtained by the hydrogen–deuterium exchange reaction of *cis*-**2a** at room temperature



cis-**2a** *cis*-**2a**-d_1 *trans*-**2a**-d_1

Compound	Time (h)							
	0	0.5	1	2	3	5	24	168
cis-**2a**	100	63.7	46.3	27.1	15.8	5.4	0	0
cis-**2a**-d_1	0	26.2	38.1	50.7	56.6	60.2	37.7	12.2
trans-**2a**-d_1	0	10.1	15.6	22.2	27.6	34.4	62.3	87.8

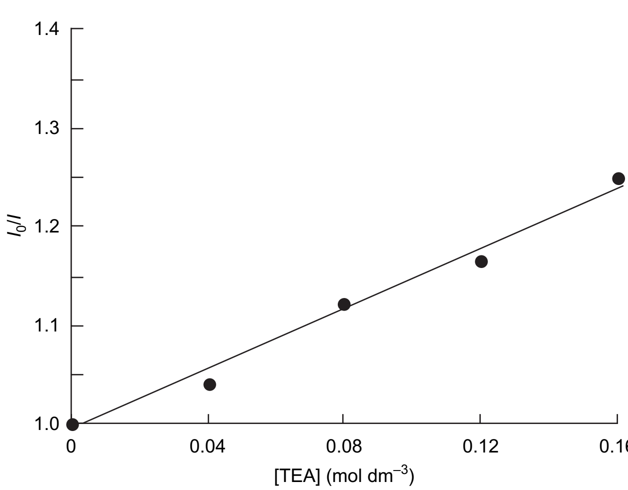


Figure 2. Stern–Volmer plot for the fluorescence quenching of (*Z*)-**1q** (1.0×10^{-4} mol dm^{-3}) by TEA in N_2-saturated MeCN at room temperature. Wavelengths for excitation and for recording emission intensities are 384 and 465 nm, respectively.

(0.76 V vs Ag/AgCl in MeCN), the reduction potential of **1a** (−2.26 V vs Ag/AgCl in MeCN), and the first singlet excitation energy of **1a** ($368\ kJ\ mol^{-1}$ in MeCN), respectively, which allowed us to estimate the free energy change (ΔG_{et}) for an ET from TEA to singlet **1a** as $-77\ kJ\ mol^{-1}$. These findings are in full agreement with the involvement of an ET in the primary process of the photocyclization reaction of **1**. In connection with the PET mechanism for this cyclization reaction, it is significant to confirm whether TEA acts as an ET catalyst during the reaction. For this confirmation a CD_3OD solution of (*Z*)-**1a** ($0.025\ mol\ dm^{-3}$) containing TEA ($0.10\ mol\ dm^{-3}$) and 1,4-dioxane (internal standard, $0.10\ mol\ dm^{-3}$) was irradiated with Pyrex-filtered light from a 450 W high-pressure Hg lamp for 4–8 h at room temperature and subjected to ^1H NMR spectral analysis. This analysis showed no sign of a change in the amine concentration and, hence, TEA was proved to be an ET catalyst.

Before we propose the PET mechanism by which the cyclization reaction of **1** proceeds to give *cis*-**2** in preference to *trans*-**2**, we should discuss the possibility of a direct ET from TEA to the *N*-acyl moiety in the excited-state (*E*)-**1**. In Figure 3 are shown UV absorption spectra of (*Z*)-**1a**, benzamide, 4-methoxybenzamide, and 4-cyanobenzamide ($1.0\times10^{-4}\ mol\ dm^{-3}$) in methanol. Clearly, benzamide and its derivatives exhibit negligible absorptions at wavelengths longer than 300 nm whereas there is a strong absorption at 320 nm in the spectrum of **1a**. It is, thus, very likely that an electron from TEA is not directly shifted to the acyl moiety but preferentially to the naphthylmethylene moiety. This consideration strongly suggests that the initially formed naphthylmethylene radical anion intramolecularly reduces the acyl group to give the corresponding acyl radical anion, the nucleophilicity of which is highly enhanced. If so, the higher electron-withdrawing ability of a substituent attached to the *para*-position on the *N*-benzoyl benzene ring is expected to reduce the fluorescence intensity of (*Z*)-**1** to a greater extent. As Figure 4 demonstrates, the finding that its emission intensity is lowered in the order of **1e** (R^2=OMe)>**1a** (R^2=H)>**1f** (R^2=CN) is consistent with the above expectation and, hence, confirms the formation of the acyl radical anion intermediate in a stepwise manner. On the basis of the considerations described above, we were

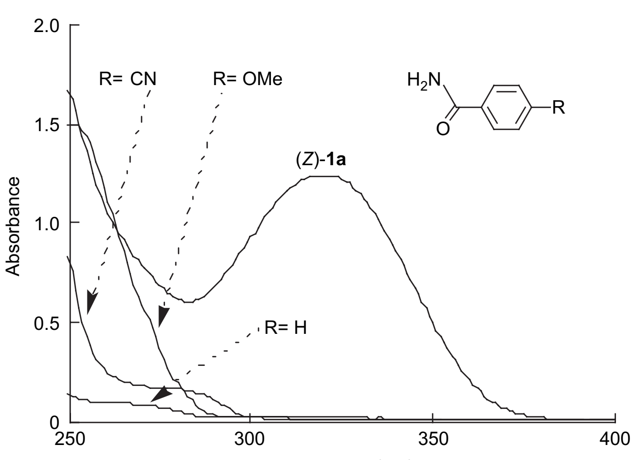


Figure 3. UV absorption spectra of (*Z*)-**1a** and 4-substituted benzamides ($1.0\times10^{-4}\ mol\ dm^{-3}$) in MeOH at room temperature.

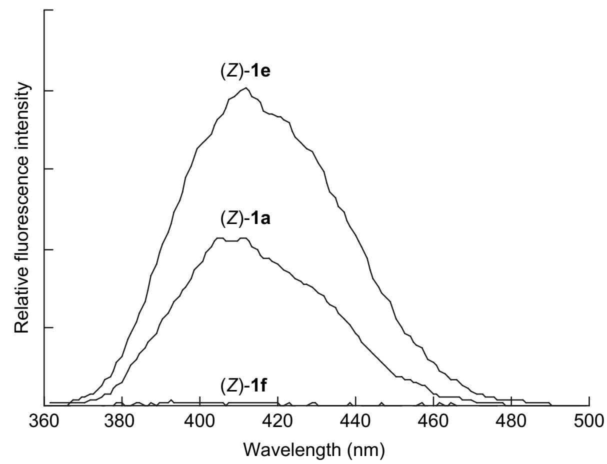
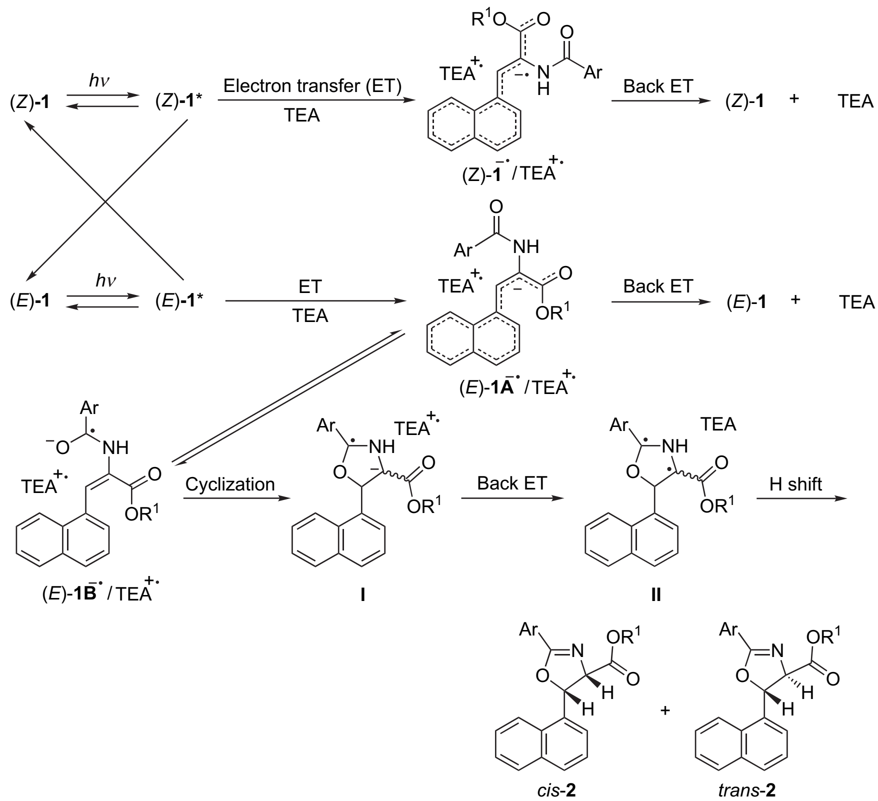


Figure 4. Fluorescence spectra of (*Z*)-**1a**, (*Z*)-**1e**, and (*Z*)-**1f** ($1.0\times10^{-4}\ mol\ dm^{-3}$) in N_2-saturated MeOH at room temperature. Excitation wavelength is 320 nm.

led to propose Scheme 2 that explains the quantitative formation of *cis*- and *trans*-dihydrooxazole derivatives (*cis*-**2** and *trans*-**2**). In addition to the principle of least motion,[12] molecular modeling of (*Z*)-**1** and (*E*)-**1** reveals that the latter isomer adopts a most suitable conformation for the cyclization reaction that eventually gives **2**. The previous finding that the triplet-sensitized reaction of (*Z*)-*N*-acyl-α-dehydrophenylalanine derivatives gives only the corresponding (*E*)-isomers without forming any cyclized products is in perfect agreement with the involvement of the singlet excited-state **1** in the ET process.[3,4] As already suggested, an ET from TEA to the singlet excited-state (*E*)-**1** results in an initial formation of the (*E*)-isomer-derived arylmethylene radical anion (*E*)-$\mathbf{1A}^{-\bullet}$, which activates the *N*-acyl carbonyl oxygen through an intramolecular ET. Accordingly, we may assume a dynamic equilibrium between these two radical anion intermediates (*E*)-$\mathbf{1A}^{-\bullet}$ and (*E*)-$\mathbf{1B}^{-\bullet}$ (see Scheme 2). In addition, the observation of the TEA-catalyzed isomerization of **2** allows us to propose the cyclized radical anion/TEA radical cation pair intermediate **I** formed by the nucleophilic attack of *N*-acyl carbonyl oxygen upon the olefinic carbon in the (*E*)-**1**-derived radical anion (*E*)-$\mathbf{1B}^{-\bullet}$.

There are two possible routes for a back ET in the radical ion pair **I**. One is the transfer of an unpaired electron from the 2-position on the dihydrooxazole ring to the TEA radical cation, which gives a zwitterion intermediate. The other is the transfer of one of the paired electrons from the 4-position on the oxazole ring to the TEA radical cation, as shown in Scheme 2. Very recently we found that the PET-initiated cyclization of bulky chiral auxiliary-substituted *N*-benzoyl-α-dehydronaphthylalanine alkyl esters affords the corresponding *cis*- and *trans*-4,5-dihydrooxazole derivatives in high diastereomeric excess (de).[13] In this study tertiary amine and temperature effects on the de value for each oxazole derivative provided a piece of evidence in support of a biradical intermediate. It is, thus, reasonable to consider that a back ET to the TEA radical cation in **I** regenerates TEA with the appearance of the biradical intermediate **II**. Owing to steric hindrance of a bulky aryl group bonded to the oxazole ring at its 5-position, hydrogen shift in **II** proceeds from the opposite side of this group to afford *cis*-**2**



Scheme 2.

in preference to *trans*-**2**, and hence the observed hydrogen shift can be regarded as a kinetically controlled process. On the other hand, an ET to the singlet excited-state (*Z*)-**1** should take place to give the (*Z*)-**1** radical anion/TEA radical cation pair intermediate, in competition with an ET to the (*E*)-isomer. However, the nucleophilic attack of *N*-acyl carbonyl oxygen upon the olefinic carbon in this intermediate undergoes a great steric hindrance of the aryl group, so that a return ET should proceed exclusively in the (*Z*)-isomer-derived radical ion pair to regenerate (*Z*)-**1** and TEA (Scheme 2).

2.3. Substituent effects in *N*-aroyl-α-dehydroarylalanine alkyl esters

For the purpose of exploring the substituent effects on the photoreactivity of **1**, the selectivity of *cis*-**2** and the extent to which the cis-isomer is isomerized to the corresponding trans-isomer, a nitrogen-saturated methanol or ethanol solution of **1b–g** (4.0×10^{-3} mol dm^{-3}, 500 mL) being irradiated in the presence of TEA (0.10 mol dm^{-3}) for a given period of time was subjected to ^{1}H NMR spectral analysis in DMSO-d_6 (Table 4). Interestingly, the introduction of a bulky alkyl substituent such as an isopropyl or a *tert*-butyl group into the alkoxycarbonyl moiety of (*Z*)-**1** produced the corresponding cis-isomer in high selectivity and, in addition, considerably suppressed the isomerization induced by TEA as a base. The suppression of this isomerization was also achieved by employing the less polar protic solvent, ethanol. Both the steric bulkiness of the alkyl group and the polarity of a given protic solvent are considered to exert great effects on the abstraction of a proton at the 4-position on the oxazole ring by TEA. On the other hand, the presence of an electron-donating methoxy or an electron-withdrawing cyano group at the 4-position on the *N*-benzoyl benzene ring lowers the excited-state reactivity of **1a** to some extent. This suggests the delocalization of an electron migrated to the *N*-aroyl moiety, namely, a decrease in the nucleophilicity of the *N*-aroyl carbonyl oxygen. Furthermore, the finding that the selectivity of *cis*-**2** decreases with increasing electron-withdrawing ability of the aryl group attached to the oxazole ring (**2e**>**2a**>**2f**) provides additional evidence for the

Table 4. Substituent effects on the conversion of **1** and selectivity of *cis*-**2**, obtained by the irradiation of (*Z*)-**1** in MeOH or EtOH at room temperature

Compound	Irradiation time (h)	Conversion[a] (%)	Composition (%)		Selectivity[b] (%)
			cis-**2**	*trans*-**2**	
1a[c]	0.5	16.5	11.5	5.0	70
	5	100	36.9	63.1	37
1b[d]	0.5	18.9	13.2	5.7	70
	5	100	68.3	31.7	68
1c[c]	0.5	18.9	16.5	2.4	87
	5	100	80.9	19.1	81
1d[c]	0.5	20.0	18.4	1.6	92
	5	100	91.5	8.5	92
1e[c]	0.5	12.6	9.8	2.8	78
	5	92.7	60.6	32.1	65
1f[c]	0.5	9.0	4.6	4.4	51
	5	75.4	13.5	61.9	18
1g[c]	0.5	8.7	5.0	3.7	57
	5	73.1	20.6	52.5	28

[a] Conversion was estimated by subtracting the sum of composition for (*Z*)-**1** and (*E*)-**1** from 100.
[b] Selectivity was estimated by dividing composition for *cis*-**2** by the sum of composition for *cis*-**2** ans *trans*-**2**.
[c] In MeOH.
[d] In EtOH. This solvent was used because of the occurrence of TEA-catalyzed ester exchange reaction in MeOH.

TEA-catalyzed isomerization of the cis-isomer to the trans. Inspection of the data in Table 4 also confirms that replacement of the 1-naphthyl group in **1a** by the phenyl (**1g**) still enables selective phototransformation into **2**, though it results in a decrease in the excited-state reactivity of **1** as well as in the selectivity of *cis*-**2**. It is very likely that the former decrease is due to the lower ability of the benzylidene group to accept an electron from TEA and the less bulky phenyl group is responsible for the latter decrease.

2.4. Substituent effects in *N*-acyl-α-dehydroarylalanine *tert*-butyl esters

The bulky *tert*-butoxycarbonyl group in *cis*-**2** was already shown to suppress the TEA-catalyzed isomerization of this isomer to a considerable extent even at 5 h irradiation (Table 4). It is thus possible to discuss quantitatively the substituent effects on the selectivity of the *cis*-4,5-dihydrooxazole isomer and to shed much light on factors, which influence not only the cis-selectivity but also the photoreactivity of **1**. In Table 5 are summarized the conversion of **1**, the compositions of *cis*-**2** and *trans*-**2**, and the selectivity of *cis*-**2**, obtained by the irradiation of (*Z*)-**1h–q** in nitrogen-saturated methanol and also included the results for (*Z*)-**1d**, for comparison. First of all, our attention is directed to the effect of substituents (introduced into the phenyl group) on the selectivity of *cis*-**2**. It is clear from the data in Table 5 that the *tert*-butyl ester derivatives **1h–n** are only subject to the very little TEA-catalyzed isomerization reactions except **1l** bearing the cyano group. Because the *para*-substituents attached to the benzene ring should exert negligible steric effects on hydrogen shift in the biradical intermediate **II**, the finding that the selectivity of *cis*-**2** is lowered in the order of MeO(**1h**)>Me(**1i**)>H(**1j**)>Cl(**1k**)>CN(**1l**) substantiates the electronic effect of a given substituent as one of the chief determining factors. The enhanced π-electron density of the benzene ring may slow down the relative rate for hydrogen shift taking place at the side of this ring owing to electronic repulsion. Interestingly, upon the introduction of methyl group at either or both of the *ortho*-positions of the benzene ring, the cis-selectivity was dramatically increased. For example, the *tert*-butyl ester derivative **1n** having two methyl groups at the *ortho*-positions underwent PET-initiated cyclization reaction to afford *cis*-**2n** selectively. This result conforms to that obtained for the 9-anthryl-substituted ester derivative **1q** and also a change in aryl substituent from 1-naphthyl (**1d**) to 2-naphthyl (**1o**) resulted in a great decrease in the cis-selectivity (92%→79%; the latter value is comparable to that of *cis*-**2i** with a 4-tolyl group). In addition, a comparison of the selectivity of *cis*-**2d** with that of *cis*-**2p** confirmed that the cis-selectivity is not practically influenced by the *N*-acyl substituent. Therefore, the considerations described above led us to conclude that the selectivity of *cis*-**2** carrying a *tert*-butoxycarbonyl group is controlled not only by the π-electron density of a substituted phenyl group attached at the 5-position on the dihydrooxazole ring but also by the steric bulkiness around the *ortho*-positions of this phenyl group.

Table 5. Substituent effects on the conversion of **1** and selectivity of *cis*-**2**, obtained by the irradiation of (*Z*)-**1** in MeOH at room temperature

Compound	Irradiation time (h)	Conversion[a] (%)	Composition (%)		Selectivity[b] (%)
			cis-**2**	*trans*-**2**	
1d	0.5	20.0	18.4	1.6	92
	3	75.0	68.9	6.1	92
1h	0.5	5.1	4.1	1.0	80
	3	30.9	24.5	6.4	79
1i	0.5	6.3	5.0	1.3	79
	3	37.1	29.0	8.1	78
1j	0.5	6.6	5.1	1.5	77
	3	40.8	31.6	9.2	77
1k	0.5	9.5	7.1	2.4	75
	3	57.6	42.5	15.1	74
1l	0.5	7.4	5.0	2.4	68
	3	42.2	23.0	19.2	55
1m	0.5	4.9	4.7	0.2	96
	3	29.8	28.5	1.3	96
1n	0.5	2.1	2.1	0	100
	3	14.0	14.0	0	100
1o	0.5	33.3	26.2	7.1	79
	3	100	78.1	21.9	78
1p	0.5	12.4	11.6	0.8	94
	3	50.7	46.9	3.8	93
1q	0.5	7.4	7.4	0	100
	3	21.1	21.1	0	100

[a] Conversion was estimated by subtracting the sum of composition for (*Z*)-**1** and (*E*)-**1** from 100.

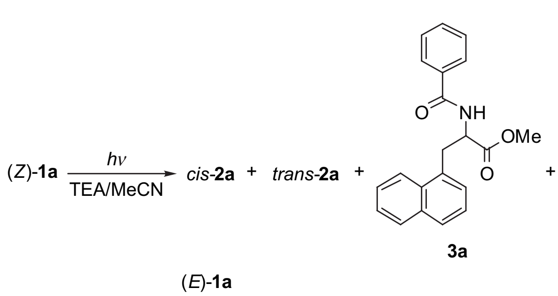
[b] Selectivity was estimated by dividing composition for *cis*-**2** by the sum of composition for *cis*-**2** ans *trans*-**2**.

Next we concentrate our attention on the more detailed substituent effects on the photoreactivity of **1** in the presence of TEA. As shown in Scheme 2, inter- and intramolecular ET reactions giving the radical anions (*E*)-**1A**$^{-\bullet}$ and (*E*)-**1B**$^{-\bullet}$, respectively, are regarded as reversible processes, so that the photoreactivity (i.e., the conversion) of **1** may be determined by the overall efficiency of these two processes, as already suggested. An increase in the stability of the initially formed radical anion (*E*)-**1A**$^{-\bullet}$ is considered to cause a decrease in the reactivity of this intermediate and, hence, to shift the equilibrium between (*E*)-**1A**$^{-\bullet}$ and (*E*)-**1B**$^{-\bullet}$ to the side of the former radical anion. Additionally, the enhanced stability of the *N*-acyl radical anion (*E*)-**1B**$^{-\bullet}$ should accelerate an intramolecular ET to the acyl moiety but diminish the nucleophilicity of the acyl carbonyl oxygen. These two effects, which are compensated by each other, are exemplified in the *N*-acyl substituent effect on the photoreactivity of **1a**, **1e**, and **1f**. Accordingly, the finding [that the reactivity of **1h–l** possessing a 4-substituted phenyl group is small and is increased in the following order: 4-OMeC$_6$H$_4$ (**1h**)<4-MeC$_6$H$_4$ (**1i**)<Ph (**1j**)<4-CNC$_6$H$_4$ (**1l**)<4-ClC$_6$H$_4$ (**1k**)] revealed that the reactivity of these derivatives is determined by the balance of consecutive inter- and intramolecular ET reaction efficiencies. The difference in reactivity between **1d** and **1p** having the *N*-benzoyl and *N*-pivaloyl groups, respectively, is also interpreted in a similar way. On the other hand, the importance of efficiency for the cyclization process yielding the intermediate **I** is found in the fact that the 2-naphthyl-substituted derivative **1o** possesses a higher photoreactivity than that of the 1-naphthyl-substituted **1d** despite almost the same electron-accepting abilities of the 1-naphthyl and 2-naphthyl groups. In other words, the latter group exerts a less steric effect on the above-mentioned cyclization process.

As already stated, the introduction of a bulky 2,6-dimethylpheny or a 9-anthryl group enabled the selective transformation into the corresponding *cis*-4,5-dihydrooxazole derivative. This finding suggests that hydrogen shift (in the intermediate **II**) giving *trans*-**2** meets with large steric hindrance exerted by both the aryl and *tert*-butoxycarbonyl groups and, hence, becomes a kinetically controlled process. The bulky aryl group should also exert a great steric hindrance toward the nucleophilic attack of the *N*-acyl carbonyl oxygen on the olefinic carbon in (*E*)-$\mathbf{1B}^{-\bullet}$. Therefore, the fact (that as in the case of **1n** with a 2,6-dimethylphenyl group, the photoreactivity of 9-anthryl-substituted **1q** is much lower than that of 1-naphthyl-substituted **1d** despite the larger electron-accepting ability of the former derivative) confirms that the bulky aryl substituent exerts a much greater steric hindrance toward the above nucleophilic attack causing a substantial decrease in the photoreactivity. While the prolonged irradiation of **1q** is responsible for undesirable side reactions, the PET-initiated cyclization of **1n** proceeded without undergoing any side reactions to selectively produce *cis*-**2n**.

2.5. Solvent effects

In a previous study we found that the change in solvent from methanol to acetonitrile affects the photoreactivity of *N*-acyl-α-dehydronaphthylalaninamide derivatives as well as the selectivity of the corresponding 3,4-dihydrobenzo[*f*]-quinolinones as major products.[5] The hydrogen-bonding solvation ability of methanol was verified to play a major role in this solvent effect. In order to explore the role of hydrogen-bonding solvation in our PET-initiated cyclization forming 4,5-dihydrooxazoles in quantitative yields, the methyl ester derivative (*Z*)-**1a** and acetonitrile were chosen as typical *N*-acyl-α-dehydronaphthylalanine alkyl ester and aprotic polar solvent, respectively. Product analysis in acetonitrile gave the unexpected result that the prolonged irradiation induces mainly the side reaction of *cis*-**2a** to afford *N*-benzoyl-1-naphthylalalanine methyl ester (**3a**), as shown in Scheme 3. This byproduct was not obtained without TEA and also in methanol containing TEA, so that the role of the protic polar solvent is considered to inhibit the dihydrooxazole ring-opening reaction through hydrogen-bonding solvation of the *cis*-**2a**-derived radical anion. In Table 6 are summarized the dependence of the product composition and the selectivity of *cis*-**2a** on irradiation time. Though the use of acetonitrile caused a side reaction of *cis*-**2a**, it suppressed TEA-catalyzed isomerization into *trans*-**2a** accompanied by a slight increase in the cis-selectivity as well as by a minor decrease in the photoreactivity. Taking into account the fact that the presence of the bulky alkoxycarbonyl group prevents the cis-isomer from isomerizing into the trans-isomer, we propose that methanol is a more suitable solvent for the reaction.



Scheme 3.

Table 6. Relation between irradiation time and composition of each compound obtained by the irradiation of (*Z*)-**1a** in MeCN containing TEA at room temperature

Irradiation time (h)	Composition (%)					*cis*-**2a**/*trans*-**2a**
	(*Z*)-**1a**	(*E*)-**1a**	*cis*-**2a**	*trans*-**2a**	**3a**	
0	100	0	0	0	0	—
0.5	41.3	49.0	7.1	2.6	0	2.7
1	36.4	43.6	14.8	5.2	0	2.8
2	26.3	31.9	30.2	11.6	0	2.6
3	16.7	20.5	42.2	17.9	2.7	2.4
5	0	0	44.1	25.2	30.7	1.8

3. Conclusions

As already described in Section 1, there are several synthetic routes to 4,5-dihydrooxazole derivatives but any convenient photochemical route to these derivatives is not yet developed. The procedure for preparing the starting (*Z*)-*N*-acyl-α-dehydroarylalanine alkyl esters (*Z*)-**1** with various types of alkyl, aryl, and acyl substituents is simple and readily applicable to their related compounds. The PET reactions of **1**, except 9-anthryl-substituted *tert*-butyl ester derivative, proceed efficiently in the presence of TEA (which is readily evacuated from the reaction mixture) to quantitatively give the corresponding *cis*- and *trans*-4,5-dihydrooxazoles without any undergoing undesirable side reactions. These two product compositions can be controlled by utilizing the steric and electronic effects of alkyl and aryl substituents introduced into (*Z*)-**1**, in addition to the amine basicity and the solvent property. Therefore, the PET-initiated cyclization reaction of **1** constitutes a novel photochemical method for the construction of a pharmaceutically useful dihydrooxazole ring.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR, and IR spectra were taken with a JEOL JNM-A500 spectrometer and a SHIMADZU PRESTIGE-21 infrared spectrometer, respectively. Chemical shifts were determined using tetramethylsilane as an internal standard. 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. Methanol, ethanol, and acetonitrile were purified according to the standard procedures[14] and distilled just before their use. TEA was fractionally distilled from sodium hydroxide. All other reagents used were obtained from commercial sources and of the highest grade available.

4.2. General procedure for the synthesis of (*Z*)-4-(1-naphthylmethylene)-2-(4-substituted phenyl)-5(4*H*)-oxazolones, (*Z*)-2-phenyl-4-(substituted benzylidene)-5(4*H*)-oxazolones, (*Z*)-4-(2-naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone, (*Z*)-2-(*tert*-butyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone, and (*Z*)-4-(9-anthrylmethylene)-2-phenyl-5(4*H*)-oxazolone

N-(4-Substituted benzoyl)glycine or trimethylacetylglycine (50 mmol), 1-naphthaldehyde, substituted benzaldehyde, 2-naphthaldehyde or anthracene-9-carbaldehyde (50 mmol), and sodium acetate (20 mmol) were added to acetic anhydride (10–30 mL) and the resulting mixture was heated at 65–75 °C for 1–2 h [*N*-(4-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 ethanol, and then with dry hexane. After the crude product was air-dried at room temperature, it was recrystallized from hexane–chloroform to give yellow crystals (40–80%).

4.2.1. (*Z*)-4-(1-Naphthylmethylene)-2-phenyl-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-Cyanophenyl)-4-(1-naphthylmethylene)-5(4*H*)-oxazolone. Mp 237.0–238.0 °C. IR (KBr): 2236, 1794, 1641, 1164 cm^{-1}. ^{1}H 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).

4.2.4. (*Z*)-4-(4-Methoxybenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 155.0–156.0 °C. IR (KBr): 1773, 1650, 1267 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (3H, s), 7.00 (2H, d, *J*=7.5 Hz), 7.22 (1H, s), 7.52 (2H, dd, *J*=6.9, 7.5 Hz), 7.59 (1H, dd, *J*=6.9, 6.9 Hz), 8.16–8.20 (4H, m).

4.2.5. (*Z*)-4-(4-Methylbenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 137.0–138.0 °C. IR (KBr): 1797, 1653, 1296 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (3H, s), 7.29 (1H, s), 7.33 (2H, d, *J*=7.9 Hz), 7.62 (2H, dd, *J*=7.3, 7.3 Hz), 7.70 (1H, dd, *J*=7.3, 7.3 Hz), 8.10 (2H, d, *J*=7.3 Hz), 8.17 (2H, d, *J*=7.9 Hz).

4.2.6. (*Z*)-4-Benzylidene-2-phenyl-5(4*H*)-oxazolone. Mp 162.0–163.0 °C. IR (KBr): 1779, 1659, 1266 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (1H, s), 7.47 (2H, dd, *J*=7.4, 8.0 Hz), 7.49 (1H, dd, *J*=7.4, 7.4 Hz), 7.54 (2H, dd, *J*=7.2, 7.4 Hz), 7.62 (1H, dd, *J*=7.4, 7.4 Hz), 8.19 (2H, d, *J*=8.0 Hz), 8.21 (2H, d, *J*=7.2 Hz).

4.2.7. (*Z*)-4-(4-Chlorobenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 192.5–193.5 °C. IR (KBr): 1797, 1770, 1656, 1236 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (1H, s), 7.43–7.63 (5H, m), 8.13–8.21 (4H, m).

4.2.8. (*Z*)-4-(4-Cyanobenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 215.0–216.0 °C. IR (KBr): 2222, 1796, 1661, 1292 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (1H, s), 7.57 (2H, dd, *J*=7.4, 8.0 Hz), 7.67 (1H, dd, *J*=7.4, 7.4 Hz), 7.75 (2H, d, *J*=8.6 Hz), 8.20 (2H, d, *J*=8.0 Hz), 8.30 (2H, d, *J*=8.6 Hz).

4.2.9. (*Z*)-4-(2-Methylbenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 134.0–135.0 °C. IR (KBr): 1788, 1643, 1200 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.53 (3H, s), 7.26 (1H, d, *J*=9.2 Hz), 7.33–7.36 (2H, m), 7.53 (2H, dd, *J*=7.4, 8.0 Hz), 7.55 (1H, s), 7.61 (1H, dd, *J*=7.4, 7.4 Hz), 8.18 (2H, d, *J*=8.0 Hz), 8.81 (1H, d, *J*=9.7 Hz).

4.2.10. (*Z*)-4-(2,6-Dimethylbenzylidene)-2-phenyl-5(4*H*)-oxazolone. Mp 112.0–113.0 °C. IR (KBr): 1798, 1663, 1171 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (6H, s), 7.12 (2H, d, *J*=7.4 Hz), 7.23 (1H, dd, *J*=7.4, 7.4 Hz), 7.48 (2H, dd, *J*=7.4, 8.0 Hz), 7.53 (1H, s), 7.59 (1H, dd, *J*=8.0, 8.0 Hz), 8.09 (2H, d, *J*=7.4 Hz).

4.2.11. (*Z*)-4-(2-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone. Mp 142.0–143.0 °C. IR (KBr): 1797, 1626, 1167 cm^{-1}. ^{1}H 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).

4.2.12. (*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}. ^{1}H 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).

4.2.13. (*Z*)-4-(9-Anthrylmethylene)-2-phenyl-5(4*H*)-oxazolone. Mp 231.0–233.0 °C. IR (KBr): 1796, 1659, 1186 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (2H, dd, *J*=7.4, 8.0 Hz), 7.50–7.56 (5H, m), 7.99 (2H, d, *J*=7.4 Hz), 8.06–8.13 (4H, m), 8.35 (1H, s), 8.57 (1H, s).

4.3. General procedure for the synthesis of alkyl (*Z*)-2-(4-substituted benzoylamino)-3-(1-naphthyl)-2-propenoates [(*Z*)-1a–f], methyl (*Z*)-2-benzoylamino-3-phenyl-2-propenoate [(*Z*)-1g], *tert*-butyl (*Z*)-3-aryl-2-benzoylamino-2-propenoates [(*Z*)-1h–o,q], and *tert*-butyl (*Z*)-3-(1-naphthyl)-2-pivaloylamino-2-propenoate [(*Z*)-1p]

(*Z*)-4-(1-Naphthylmethylene)-2-(4-substituted phenyl)-5(4*H*)-oxazolone (for **1a–f**, 10 mmol), (*Z*)-2-phenyl-4-(substituted benzylidene)-5(4*H*)-oxazolone (for **1g–n**, 10 mmol), (*Z*)-4-(2-naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone (for **1o**, 10 mmol), (*Z*)-2-*tert*-butyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1p**, 10 mmol), or (*Z*)-4-(9-anthrylmethylene)-2-phenyl-5(4*H*)-oxazolone (for **1q**, 10 mmol) were added to a given alcohol (60 mL) containing TEA or DBU (5.0 mmol) and the resulting solution was refluxed for 1–2 h. After removal of the solvent under reduced pressure, the reaction mixture obtained was dissolved in chloroform (50–100 mL) and then washed twice with hydrochloric acid (3 mol dm^{-3}, 50 mL), and finally dried over sodium sulfate. Evaporation of chloroform in vacuo gave the crystalline solid, which was recrystallized from ethyl acetate–hexane affording colorless crystals (30–90%). Before recrystallization some of the crude alkyl 2-acylamino-3-aryl-2-propenoates were chromatographed on a silica gel column with ethyl acetate–chloroform or ethyl acetate–hexane as an eluent for preliminary purification.

4.3.1. Methyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1a]. Mp 118.0–118.5 °C. IR (KBr): 3200, 1732, 1632 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.80 (3H, s), 7.46 (2H, dd, J=7.6, 7.6 Hz), 7.51 (1H, dd, J=7.6, 8.9 Hz), 7.55 (1H, dd, J=7.6, 7.6 Hz), 7.58 (1H, dd, J=6.9, 6.9 Hz), 7.59 (1H, dd, J=6.9, 7.6 Hz), 7.69 (1H, d, J=7.6 Hz), 7.84 (2H, d, J=7.6 Hz), 7.90 (1H, s), 7.94 (1H, d, J=8.9 Hz), 7.97 (1H, d, J=6.9 Hz), 8.05 (1H, d, J=7.6 Hz), 10.0 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 52.3, 124.1, 125.4, 126.2, 126.62, 126.65, 127.6 (2C), 128.3 (2C), 128.5, 128.9, 129.2, 129.9, 130.5, 131.0, 131.8, 133.15, 133.22, 165.3, 166.4. Anal. Calcd (found) for $C_{21}H_{17}NO_3$: C, 76.12 (75.88); H, 5.17 (4.98); N, 4.23% (4.19%).

4.3.2. Ethyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1b]. Mp 108.0–109.0 °C. IR (KBr): 3250, 1720, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.29 (3H, t, J=6.9 Hz), 4.26 (2H, q, J=6.9 Hz), 7.46 (2H, dd, J=7.6, 7.6 Hz), 7.51 (1H, dd, J=7.6, 7.6 Hz), 7.55 (1H, dd, J=7.6, 7.6 Hz), 7.57 (1H, dd, J=6.9, 6.9 Hz), 7.59 (1H, dd, J=6.9, 7.6 Hz), 7.70 (1H, d, J=7.6 Hz), 7.84 (2H, d, J=7.6 Hz), 7.90 (1H, s), 7.94 (1H, d, J=7.6 Hz), 7.97 (1H, d, J=6.9 Hz), 8.05 (1H, d, J=7.6 Hz), 9.98 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 14.1, 61.0, 124.1, 125.4, 126.2, 126.7 (2C), 127.6 (2C), 128.4 (2C), 128.5, 128.2, 129.3, 129.6, 130.5, 131.0, 131.8, 133.2, 133.4, 164.8, 166.5. Anal. Calcd (found) for $C_{22}H_{19}NO_3$: C, 76.50 (76.18); H, 5.54 (5.46); N, 4.06% (3.99%).

4.3.3. Isopropyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1c]. Mp 89.0–90.0 °C. IR (KBr): 3240, 1721, 1638 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.28 (6H, d, J=6.2 Hz), 5.06 (1H, q, J=6.2 Hz), 7.46 (2H, dd, J=7.6, 8.2 Hz), 7.51 (1H, dd, J=6.9, 8.2 Hz), 7.55 (1H, dd, J=6.9, 8.6 Hz), 7.56 (1H, dd, J=6.9, 7.6 Hz), 7.59 (1H, dd, J=8.2, 8.2 Hz), 7.70 (1H, d, J=6.9 Hz), 7.82 (2H, d, J=7.6 Hz), 7.85 (1H, s), 7.93 (1H, d, J=8.2 Hz), 7.97 (1H, d, J=8.6 Hz), 8.02 (1H, d, J=7.6 Hz), 9.96 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 21.6 (2C), 68.5, 124.1, 125.4, 126.2, 126.6, 126.7, 127.5 (2C), 128.3 (2C), 128.5, 129.07, 129.11, 129.7, 130.6, 130.9, 131.7, 133.2, 133.5, 164.3, 166.5. Anal. Calcd (found) for $C_{23}H_{21}NO_3$: C, 76.86 (76.82); H, 5.89 (5.62); N, 3.90% (3.81%).

4.3.4. *tert*-Butyl (*Z*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*Z*)-1d]. Mp 120.0–121.0 °C. IR (KBr): 3289, 1709, 1638 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.50 (9H, s), 7.45 (2H, dd, J=7.6, 8.2 Hz), 7.50 (1H, dd, J=6.9, 8.2 Hz), 7.54 (1H, dd, J=7.6, 7.6 Hz), 7.58 (1H, dd, J=6.9, 8.2 Hz), 7.59 (1H, dd, J=6.9, 7.6 Hz), 7.68 (1H, d, J=6.9 Hz), 7.81 (2H, d, J=8.2 Hz), 7.82 (1H, s), 7.92 (1H, d, J=8.2 Hz), 7.96 (1H, d, J=7.6 Hz), 8.01 (1H, d, J=8.2 Hz), 9.88 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 27.6 (3C), 80.7, 124.0, 125.4, 126.0, 126.5 (2C), 127.5 (2C), 128.2 (2C), 128.4, 128.6, 128.9, 130.4, 130.7, 130.9, 131.5, 133.1, 133.6, 163.7, 166.5. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (77.35); H, 6.21 (6.29); N, 3.75% (3.74%).

4.3.5. Methyl (*Z*)-2-(4-methoxybenzoylamino)-3-(1-naphthyl)-2-propenoate [(*Z*)-1e]. Mp 137.0–138.0 °C. IR (KBr): 3275, 1717, 1639 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.79 (3H, s), 3.80 (3H, s), 6.99 (2H, d, J=8.6 Hz), 7.49 (1H, dd, J=6.9, 8.6 Hz), 7.55–7.59 (2H, m), 7.67 (1H, d, J=6.9 Hz), 7.84 (2H, d, J=8.6 Hz), 7.87 (1H, s), 7.92 (1H, d, J=8.6 Hz), 7.96–7.98 (1H, m), 8.02–8.04 (1H, m), 9.84 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 52.2, 55.3, 113.5 (2C), 124.0, 125.28, 125.34, 126.1, 126.5, 126.6, 128.4, 129.0, 129.1, 129.2, 129.5 (2C), 130.5, 130.9, 133.1, 162.0, 165.4, 165.7. Anal. Calcd (found) for $C_{22}H_{19}NO_4$: C, 73.12 (73.01); H, 5.30 (5.16); N, 3.88% (3.81%).

4.3.6. Methyl (*Z*)-2-(4-cyanobenzoylamino)-3-(1-naphthyl)-2-propenoate [(*Z*)-1f]. Mp 166.5–167.5 °C. IR (KBr): 3325, 2230, 1709, 1626 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.80 (3H, s), 7.51 (1H, dd, J=7.4, 8.0 Hz), 7.55–7.61 (2H, m), 7.67 (1H, d, J=7.4 Hz), 7.94–7.99 (7H, m), 8.02 (1H, d, J=8.0 Hz), 10.27 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 52.4, 114.2, 118.2, 124.1, 125.5, 126.3, 126.68, 126.73, 128.4 (2C), 128.6, 129.4, 130.3, 130.7 (2C), 130.9, 132.5 (2C), 133.2, 137.1, 165.0 (2C). Anal. Calcd (found) for $C_{22}H_{16}N_2O_3$: C, 74.15 (74.12); H, 4.59 (4.62); N, 7.86% (7.86%).

4.3.7. Methyl (*Z*)-2-benzoylamino-3-phenyl-2-propenoate [(*Z*)-1g]. Mp 139.0–140.0 °C. IR (KBr): 3333, 1715, 1643 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.74 (3H, s), 7.37 (1H, dd, J=7.4, 7.4 Hz), 7.41 (2H, dd, J=6.9, 7.4 Hz), 7.43 (1H, s), 7.54 (2H, dd, J=7.4, 7.4 Hz), 7.61 (1H, dd, J=7.4, 7.4 Hz), 7.68 (2H, d, J=6.9 Hz), 7.99 (2H, d, J=7.4 Hz), 10.11 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ 52.2, 126.5, 127.6 (2C), 128.4 (2C), 128.6 (2C), 129.5, 129.8 (2C), 131.8, 133.10, 133.12, 133.3, 165.4, 166.0. Anal. Calcd (found) for $C_{17}H_{15}NO_3$: C, 72.58 (72.43); H, 5.37 (5.46); N, 4.98% (5.10%).

4.3.8. *tert*-Butyl (*Z*)-2-benzoylamino-3-(4-methoxyphenyl)-2-propenoate [(*Z*)-1h]. Mp 155.0–156.0 °C. IR (KBr): 3304, 1715, 1647 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.44 (9H, s), 3.76 (3H, s), 6.96 (2H, d, J=9.2 Hz), 7.31 (1H, s), 7.53 (2H, dd, J=7.4, 8.0 Hz), 7.59 (1H, dd, J=7.4, 7.4 Hz), 7.63 (2H, d, J=9.2 Hz), 7.96 (2H, d, J=8.0 Hz), 9.86 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.7 (3C), 55.2, 80.3, 114.1 (2C), 125.8, 126.1 (2C), 127.6 (2C), 128.4 (2C), 131.58, 131.63, 132.4, 133.8, 160.1, 164.2, 166.2. Anal. Calcd (found) for $C_{21}H_{23}NO_4$: C, 71.37 (71.01); H, 6.56 (6.58); N, 3.96% (3.94%).

4.3.9. *tert*-Butyl (*Z*)-2-benzoylamino-3-(4-methylphenyl)-2-propenoate [(*Z*)-1i]. Mp 150.0–151.0 °C. IR (KBr): 3298, 1718, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.44 (9H, s), 2.29 (3H, s), 7.20 (2H, d, J=7.5 Hz), 7.30 (1H, s), 7.51–7.56 (4H, m), 7.59 (1H, dd, J=7.5, 7.5 Hz), 7.96 (2H, d, J=7.5 Hz), 9.91 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.9, 27.6 (3C), 80.5, 127.3, 127.6 (2C), 128.4 (2C), 129.2 (2C), 129.7 (2C), 130.9, 131.7, 132.2, 133.7, 139.1, 164.1, 166.2. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.33); H, 6.87 (6.53); N, 4.15% (4.37%).

4.3.10. *tert*-Butyl (*Z*)-2-benzoylamino-3-phenyl-2-propenoate [(*Z*)-1j]. Mp 144.0–145.0 °C. IR (KBr): 3248, 1709, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.44 (9H, s), 7.31 (1H, s), 7.34 (1H, dd, J=7.5, 7.5 Hz), 7.40 (2H, dd, J=7.5, 7.5 Hz), 7.51 (2H, dd, J=7.5, 7.5 Hz), 7.60 (1H, dd, J=7.5, 7.5 Hz), 7.65 (2H, d, J=7.5 Hz), 7.95 (2H, d, J=7.5 Hz), 9.98 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.1 (3C), 80.1, 127.1 (2C), 127.7, 127.9 (2C), 128.1 (2C), 128.7, 129.2 (2C), 131.2, 131.4, 133.15, 133.19, 163.5, 165.8. Anal. Calcd (found) for $C_{20}H_{21}NO_3$: C, 74.28 (74.11); H, 6.55 (6.21); N, 4.33% (4.43%).

4.3.11. *tert*-Butyl (*Z*)-2-benzoylamino-3-(4-chlorophenyl)-2-propenoate [(*Z*)-1k]. Mp 171.0–172.0 °C. IR (KBr): 3281, 1709, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.44 (9H, s), 7.29 (1H, s), 7.47 (2H, d, J=7.4 Hz), 7.53 (2H, dd, J=7.4, 7.4 Hz), 7.60 (1H, dd, J=7.4, 7.4 Hz), 7.66 (2H, d, J=8.6 Hz), 7.94 (2H, d, J=8.6 Hz), 9.98 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 80.8, 127.6 (2C), 128.4 (2C), 128.6 (2C), 128.8, 130.3, 131.3 (2C), 131.8, 132.7, 133.5, 133.6, 163.9, 166.3. Anal. Calcd (found) for $C_{20}H_{20}ClNO_3$: C, 67.13 (67.20); H, 5.63 (5.34); N, 3.91% (3.99%).

4.3.12. *tert*-Butyl (*Z*)-2-benzoylamino-3-(4-cyanophenyl)-2-propenoate [(*Z*)-1l]. Mp 160.0–161.0 °C. IR (KBr): 3264, 2230, 1709, 1657 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.45 (9H, s), 7.29 (1H, s), 7.53 (2H, dd, J=7.5, 7.5 Hz), 7.61 (1H, dd, J=7.5, 7.5 Hz), 7.80 (2H, d, J=7.5 Hz), 7.86 (2H, d, J=8.6 Hz), 7.93 (2H, d, J=8.6 Hz), 10.1 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.9, 27.6 (3C), 80.6, 127.1 (2C), 127.4, 127.6 (2C), 128.3 (2C), 129.5, 131.2, 131.6, 133.0, 133.8, 136.0 (2C), 163.5, 166.1. Anal. Calcd (found) for $C_{21}H_{20}N_2O_3$: C, 72.40 (72.16); H, 5.79 (5.45); N, 8.04% (8.01%).

4.3.13. *tert*-Butyl (*Z*)-2-benzoylamino-3-(2-methylphenyl)-2-propenoate [(*Z*)-1m]. Mp 157.0–158.0 °C. IR (KBr): 3296, 1711, 1643 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.43 (9H, s), 2.31 (3H, s), 7.14 (1H, dd, J=6.9, 6.9 Hz), 7.19–7.25 (2H, m), 7.38 (1H, s), 7.46–7.49 (3H, m), 7.55 (1H, dd, J=7.4, 7.4 Hz), 7.85 (2H, d, J=7.4 Hz), 9.83 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.9, 27.9 (3C), 80.9, 126.0, 127.9 (2C), 128.4, 128.7 (2C), 129.0, 129.3, 130.37, 130.44, 131.9, 133.1, 134.0, 137.4, 164.2, 166.7. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.43); H, 6.87 (6.79); N, 4.15% (4.18%).

4.3.14. *tert*-Butyl (*Z*)-2-benzoylamino-3-(2,6-dimethylphenyl)-2-propenoate [(*Z*)-1n]. Mp 120.0–121.0 °C. IR (KBr): 3362, 1721, 1667 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.45 (9H, s), 2.15 (6H, s), 7.01 (2H, d, J=7.4 Hz), 7.08 (1H, dd, J=8.0, 8.0 Hz), 7.13 (1H, s), 7.44 (2H, dd, J=7.4, 8.0 Hz), 7.53 (1H, dd, J=7.4, 7.4 Hz), 7.74 (2H, d, J=7.4 Hz), 9.56 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.8 (2C), 28.5 (3C), 81.5, 128.0 (2C), 128.3, 128.5 (2C), 129.2 (2C), 130.4, 132.1, 132.5, 133.9, 134.7, 136.9 (2C), 164.4, 167.0. Anal. Calcd (found) for $C_{22}H_{25}NO_3$: C, 75.19 (74.82); H, 7.17 (7.34); N, 3.99% (3.83%).

4.3.15. *tert*-Butyl (*Z*)-2-benzoylamino-3-(2-naphthyl)-2-propenoate [(*Z*)-1o]. Mp 169.0–170.0 °C. IR (KBr): 3323, 1707, 1660 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.48 (9H, s), 7.49 (1H, s), 7.51–7.56 (4H, m), 7.61 (1H, dd, J=7.4, 7.4 Hz), 7.82 (1H, d, J=8.6 Hz), 7.86–7.91 (3H, m), 7.98 (2H, d, J=7.4 Hz), 8.19 (1H, s), 10.1 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.5 (3C), 81.5, 126.9, 127.4, 127.9, 128.3, 128.4 (2C), 128.7, 129.1, 129.2, 129.3 (2C), 131.1, 132.2, 132.6, 132.7, 133.5, 133.8, 134.5, 164.9, 167.2. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (77.02); H, 6.21 (6.19); N, 3.75% (3.70%).

4.3.16. *tert*-Butyl (*Z*)-3-(1-naphthyl)-2-pivaloylamino-2-propenoate [(*Z*)-1p]. Mp 154.0–155.0 °C. IR (KBr): 3271, 1703, 1639 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.07 (9H, s), 1.48 (9H, s), 7.51 (1H, dd, J=7.6, 8.2 Hz), 7.56–7.57 (2H, m), 7.61 (1H, d, J=7.6 Hz), 7.68 (1H, s), 7.91–7.97 (3H, m), 8.94 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.9 (3C), 26.9 (3C), 38.1, 80.4, 124.1, 125.3, 126.0, 126.5, 126.8, 127.7, 128.5, 128.9, 130.8 (2C), 131.0, 133.2, 164.1, 177.2. Anal. Calcd (found) for $C_{22}H_{27}NO_3$: C, 74.76 (74.66); H, 7.70 (7.70); N, 3.96% (4.18%).

4.3.17. *tert*-Butyl (*Z*)-3-(9-anthryl)-2-benzoylamino-2-propenoate [(*Z*)-1q]. Mp 166.0–167.0 °C. IR (KBr): 3323, 1692, 1670 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.54 (9H, s), 7.29 (2H, dd, J=7.4, 7.4 Hz), 7.41 (1H, dd, J=7.4, 7.4 Hz), 7.46–7.51 (6H, m), 7.87 (1H, s), 8.04 (2H, d, J=7.4 Hz), 8.09 (2H, d, J=7.4 Hz), 8.61 (1H, s), 9.62 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.0 (3C), 81.1, 125.6 (2C), 125.8, 126.0 (2C), 126.3 (2C), 127.7 (2C), 127.9, 128.0, 128.3 (2C), 129.0 (3C), 131.1 (2C), 131.7, 133.7, 134.1 (2C), 163.7, 166.9. Anal. Calcd (found) for $C_{28}H_{25}NO_3$: C, 79.41 (79.10); H, 5.95 (5.91); N, 3.31% (3.22%).

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

In order to examine the dependence of the product distribution and composition on irradiation time, a nitrogen-saturated methanol solution of (*Z*)-**1** (4.0×10^{-3} mol dm^{-3}, 500 mL) containing TEA (0.10 mol dm^{-3}), placed in a Pyrex vessel, was irradiated with Pyrex-filtered light from a 400 W high-pressure Hg lamp at room temperature (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 ^{1}H NMR spectral analysis. 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 column chromatography over silica gel (230 mesh, Merck) eluting with chloroform–ethyl acetate or hexane–ethyl acetate. Preparative TLC plate (silica gel) was also used for isolating the photoproducts.

For the purpose of analyzing the effect of TEA concentration on the photoreactivity of **1a** and the product composition, nitrogen-saturated methanol solutions of (*Z*)-**1a** (4.0×10^{-3} mol dm^{-3}, 10 mL) containing varying amounts of TEA, placed in sealed Pyrex tubes, were irradiated in parallel for 3 h with Pyrex-filtered light from a 400 W high-pressure Hg lamp set in a Pyrex cooling jacket (external irradiation). Parallel irradiation of the solutions was carried out at room temperature on a merry-go-round-type irradiation equipment immersed into a water bath (RIKO model RH400-10W). After the irradiation, each solution was concentrated to dryness in vacuo. The resulting residue was dissolved in DMSO-d_6 and subjected to ^{1}H NMR spectral analysis.

Physical and spectroscopic data of *cis*-4,5-dihydrooxazoles (*cis*-**2**), *trans*-4,5-dihydrooxazoles (*trans*-**2**), (*E*)-**1**, and 1-naphthylalanine derivative (**3a**) isolated are as follows.

4.4.1. Methyl (*E*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*E*)-1a]. Mp 156.0–157.0 °C. IR (KBr): 3240, 1736, 1632 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.47 (3H, s), 7.32 (1H, d, J=7.4 Hz), 7.34 (1H, s), 7.49 (1H, dd, J=7.4, 8.0 Hz), 7.55–7.61 (2H, m), 7.57 (2H, dd, J=7.4, 8.6 Hz), 7.64 (1H, dd, J=7.4, 7.4 Hz), 7.90 (1H, d, J=8.0 Hz), 7.95–7.98 (1H, m), 8.00 (2H, d, J=8.6 Hz), 8.02–8.04 (1H, m), 10.7 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 51.7, 120.0, 124.3, 125.5, 125.7, 126.2, 126.5, 127.8 (2C), 128.1, 128.5, 128.6 (2C), 131.0, 131.1, 131.6, 132.2, 132.8, 133.1, 165.09, 165.10. Anal. Calcd (found) for $C_{21}H_{17}NO_3$: C, 76.12 (76.02); H, 5.17 (5.26); N, 4.23% (4.09%).

4.4.2. *tert*-Butyl (*E*)-2-benzoylamino-3-(1-naphthyl)-2-propenoate [(*E*)-1d]. Mp 163.0–164.0 °C. IR (KBr): 3198, 1724, 1628 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.02 (9H, s), 7.24 (1H, s), 7.35 (1H, d, J=6.9 Hz), 7.50 (1H, dd, J=6.9, 8.2 Hz), 7.54–7.57 (2H, m), 7.56 (2H, dd, J=7.6, 7.6 Hz), 7.63 (1H, dd, J=7.6, 7.6 Hz), 7.90 (1H, d, J=8.2 Hz), 7.90–8.10 (2H, m), 7.98 (2H, d, J=7.6 Hz), 10.51 (1H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.0 (3C), 80.4, 120.1, 124.8, 125.2, 125.99, 126.01, 126.2, 127.69, 127.72 (2C), 128.2, 128.5 (2C), 131.2, 132.0, 132.5, 132.85, 132.94, 133.2, 163.0, 165.0. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (77.09); H, 6.21 (6.32); N, 3.75% (3.73%).

4.4.3. *cis*-4-Methoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2a). Mp 133.0–134.0 °C. IR (KBr): 1742, 1646 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.72 (3H, s), 5.62 (1H, d, J=10.3 Hz), 6.88 (1H, d, J=10.3 Hz), 7.51–7.52 (2H, m), 7.57 (1H, dd, J=7.4, 7.4 Hz), 7.59 (2H, dd, J=7.4, 7.7 Hz), 7.60 (1H, dd, J=7.4, 8.7 Hz), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.90–7.92 (1H, m), 7.96 (1H, d, J=7.4 Hz), 8.08 (2H, d, J=7.7 Hz), 8.10 (1H, d, J=8.7 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 50.7, 72.7, 80.0, 122.9, 123.6, 125.1, 125.9, 126.2, 126.4, 128.2 (2C), 128.3, 128.4, 128.9 (2C), 129.7, 132.0, 132.3, 132.8, 165.2, 169.0. Anal. Calcd (found) for $C_{21}H_{17}NO_3$: C, 76.12 (75.89); H, 5.17 (5.20); N, 4.23% (4.48%).

4.4.4. *trans*-4-Methoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2a). Mp 108.0–109.0 °C. IR (KBr): 1742, 1640 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.81 (3H, s), 4.89 (1H, d, J=6.9 Hz), 6.70 (1H, d, J=6.9 Hz), 7.52 (1H, d, J=7.4 Hz), 7.54 (1H, dd, J=6.9, 7.4 Hz), 7.57 (2H, dd, J=7.4, 7.4 Hz), 7.62 (1H, dd, J=8.6, 9.2 Hz), 7.62 (1H, dd, J=6.3, 9.2 Hz), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.98 (1H, d, J=6.9 Hz), 8.00 (1H, d, J=8.6 Hz), 8.04 (1H, d, J=6.3 Hz), 8.05 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 53.3, 75.8, 81.2, 123.3, 123.7, 126.1, 126.8, 126.9, 127.4, 128.9 (2C), 129.5 (2C), 129.6, 129.7, 130.0, 133.0, 134.1, 135.0, 165.1, 171.5. Anal. Calcd (found) for $C_{21}H_{17}NO_3$: C, 76.12 (76.14); H, 5.17 (5.21); N, 4.23% (4.09%).

4.4.5. *cis*-4-Ethoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2b). Mp 100.0–101.0 °C. IR (KBr): 1738, 1651 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.12 (3H, dd, J=6.9, 6.9 Hz), 3.09 (1H, dq, J=6.9, 10.3 Hz), 3.33 (1H, dq, J=6.9, 10.3 Hz), 5.60 (1H, d, J=10.3 Hz), 6.88 (1H, d, J=10.3 Hz), 7.50 (1H, dd, J=6.9, 7.4 Hz), 7.52 (1H, d, J=7.4 Hz), 7.58 (1H, dd, J=8.0, 9.2 Hz), 7.59 (2H, dd, J=7.4, 7.4 Hz), 7.61 (1H, dd, J=8.0, 9.2 Hz), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.91 (1H, d, J=6.9 Hz), 7.97 (1H, d, J=8.0 Hz), 8.08 (2H, d, J=7.4 Hz), 8.12 (1H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 12.5, 59.7, 72.4, 80.1, 123.0, 123.8, 125.1, 125.9, 126.2, 126.7, 128.2 (2C), 128.3, 128.4, 128.9 (2C), 129.9, 132.1, 132.3, 132.9, 165.1, 168.6. Anal. Calcd (found) for $C_{22}H_{19}NO_3$: C, 76.50 (75.92); H, 5.54 (5.81); N, 4.06% (3.94%).

4.4.6. *trans*-4-Ethoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2b). Oily liquid. IR (NaCl): 1734, 1645 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.28 (3H, dd, J=6.9, 6.9 Hz), 4.24 (1H, dq, J=6.9, 10.3 Hz), 4.30 (1H, dq, J=6.9, 10.3 Hz), 4.83 (1H, d, J=6.3 Hz), 6.69 (1H, d, J=6.3 Hz), 7.52 (1H, dd, J=7.4, 8.0 Hz), 7.53 (1H, d, J=8.0 Hz), 7.58 (2H, dd, J=7.4, 8.0 Hz), 7.61–7.63 (2H, m), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.98 (1H, d, J=7.4 Hz), 8.00 (1H, d, J=8.6 Hz), 8.06 (2H, d, J=8.0 Hz), 8.04 (1H, d, J=9.7 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.0, 61.5, 75.4, 80.6, 122.7, 123.0, 125.5, 126.2, 126.3, 126.8, 128.3 (2C), 128.95 (2C), 129.00, 129.04, 129.3, 132.4, 133.5, 134.6, 164.5, 170.5. Anal. Calcd (found) for $C_{22}H_{19}NO_3$: C, 76.50 (76.34); H, 5.54 (5.36); N, 4.06% (4.36%).

4.4.7. *cis*-4-Isopropoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2c). Mp 132.5–133.5 °C. IR (KBr): 1730, 1653 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ −0.15 (3H, d, J=6.3 Hz), 0.69 (3H, d, J=6.3 Hz), 4.07 (1H, qq, J=6.3, 6.3 Hz), 5.56 (1H, d, J=10.3 Hz), 6.84 (1H, d, J=10.3 Hz), 7.50 (1H, dd, J=7.4, 7.4 Hz), 7.54 (1H, d, J=7.4 Hz), 7.57 (1H, dd, J=7.4, 8.0 Hz), 7.59 (2H, dd, J=7.4, 8.0 Hz), 7.61 (1H, dd, J=7.4, 8.0 Hz), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.90 (1H, d, J=7.4 Hz), 7.96 (1H, d, J=8.0 Hz), 8.07 (2H, d, J=8.0 Hz), 8.11 (1H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.5, 21.0, 67.4, 72.3, 80.2, 123.1, 123.9, 125.2, 125.9, 126.2, 126.7, 128.2 (2C), 128.3, 128.4, 128.9 (2C), 130.0, 132.0, 132.3, 133.0, 165.0, 168.1. Anal. Calcd (found) for $C_{23}H_{21}NO_3$: C, 76.86 (76.86); H, 5.89 (6.12); N, 3.90% (3.79%).

4.4.8. *trans*-4-Isopropoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2c). Oily liquid. IR (NaCl): 1734, 1647 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (3H, d, J=6.3 Hz), 1.31 (3H, d, J=5.7 Hz), 4.74 (1H, d, J=6.9 Hz), 5.10 (1H, qq, J=5.7, 6.3 Hz), 6.66 (1H, d, J=6.9 Hz), 7.51 (1H, d, J=6.3 Hz), 7.54 (1H, dd, J=6.3, 8.6 Hz), 7.58 (2H, dd, J=7.4, 7.4 Hz), 7.60–7.62

(2H, m), 7.67 (1H, dd, J=7.4, 7.4 Hz), 7.97 (1H, d, J=8.6 Hz), 7.97 (1H, d, J=8.6 Hz), 8.04 (1H, d, J=8.3 Hz), 8.06 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 21.4, 21.5, 69.2, 75.7, 80.7, 122.7, 122.9, 125.5, 126.2, 126.4, 126.7, 128.3 (2C), 128.97 (3C), 129.05, 129.2, 132.4, 133.5, 134.7, 164.5, 170.0. Anal. Calcd (found) for $C_{23}H_{21}NO_3$: C, 76.86 (76.82); H, 5.89 (5.98); N, 3.90% (3.79%).

4.4.9. *cis*-4-*tert*-Butoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2d). Mp 144.0–145.0 °C. IR (KBr): 1737, 1649 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.50 (9H, s), 5.48 (1H, d, J=10.3 Hz), 6.81 (1H, d, J=10.3 Hz), 7.51 (1H, d, J=8.2 Hz), 7.54 (1H, dd, J=7.6, 8.2 Hz), 7.58 (1H, dd, J=7.6, 7.6 Hz), 7.58 (2H, dd, J=6.9, 7.6 Hz), 7.62 (1H, dd, J=7.6, 8.2 Hz), 7.66 (1H, dd, J=7.6, 7.6 Hz), 7.93 (1H, d, J=7.6 Hz), 7.98 (1H, d, J=7.6 Hz), 8.07 (2H, d, J=6.9 Hz), 8.11 (1H, d, J=8.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.4 (3C), 72.5, 80.0, 80.2, 123.1, 124.0, 125.2, 125.9, 126.1, 126.8, 128.1 (2C), 128.31, 128.33, 128.8 (2C), 130.2, 132.1, 132.3, 133.0, 164.8, 167.6. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (77.30); H, 6.21 (6.03); N, 3.75% (3.65%).

4.4.10. *trans*-4-*tert*-Butoxycarbonyl-5-(1-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2d). Oily liquid. IR (NaCl): 1728, 1647 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.51 (9H, s), 4.65 (1H, d, J=6.2 Hz), 6.61 (1H, d, J=6.2 Hz), 7.50 (1H, d, J=6.9 Hz), 7.54 (1H, dd, J=6.9, 6.9 Hz), 7.58 (2H, dd, J=7.6, 7.6 Hz), 7.60–7.63 (2H, m), 7.67 (1H, dd, J=7.6, 7.6 Hz), 7.97 (1H, d, J=6.9 Hz), 7.97 (1H, d, J=6.9 Hz), 8.03–8.06 (1H, m), 8.06 (2H, d, J=7.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 76.4, 80.8, 82.1, 122.7, 122.8, 125.5, 126.2, 126.4, 126.6, 128.3 (2C), 128.92, 128.94 (2C), 129.0, 129.1, 132.4, 133.5, 134.7, 164.4, 169.6. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (76.94); H, 6.21 (5.96); N, 3.75% (3.57%).

4.4.11. *cis*-4-Methoxycarbonyl-2-(4-methoxyphenyl)-5-(1-naphthyl)-4,5-dihydrooxazole (*cis*-2e). Mp 158.0–159.0 °C. IR (KBr): 1744, 1651 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.71 (3H, s), 3.86 (3H, s), 5.56 (1H, d, J=10.3 Hz), 6.84 (1H, d, J=10.3 Hz), 7.12 (2H, d, J=8.9 Hz), 7.49 (1H, d, J=7.6 Hz), 7.51 (1H, dd, J=6.9, 7.6 Hz), 7.56 (1H, dd, J=7.6, 8.2 Hz), 7.59 (1H, dd, J=7.6, 8.2 Hz), 7.90 (1H, d, J=6.9 Hz), 7.96 (1H, d, J=8.2 Hz), 8.01 (2H, d, J=8.9 Hz), 8.09 (1H, d, J=8.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 50.7, 55.5, 72.7, 79.8, 114.2 (2C), 118.9, 122.9, 123.6, 125.1, 125.8, 126.1, 128.3, 128.4, 129.7, 130.7 (2C), 132.1, 132.8, 162.3, 165.0, 169.2. Anal. Calcd (found) for $C_{22}H_{19}NO_4$: C, 73.12 (72.75); H, 5.30 (5.38); N, 3.88% (3.74%).

4.4.12. *trans*-4-Methoxycarbonyl-2-(4-methoxyphenyl)-5-(1-naphthyl)-4,5-dihydrooxazole (*trans*-2e). Mp 116.5–117.5 °C. IR (KBr): 1719, 1647 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.80 (3H, s), 3.85 (3H, s), 4.82 (1H, d, J=6.9 Hz), 6.64 (1H, d, J=6.9 Hz), 7.10 (2H, d, J=8.2 Hz), 7.49 (1H, d, J=6.9 Hz), 7.53 (1H, dd, J=6.9, 8.2 Hz), 7.60 (1H, dd, J=6.9, 7.9 Hz), 7.63 (1H, dd, J=6.9, 8.2 Hz), 7.97 (1H, d, J=8.2 Hz), 7.97 (1H, d, J=7.9 Hz), 7.99 (2H, d, J=8.2 Hz), 8.03 (1H, d, J=8.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 52.7, 55.5, 75.2, 80.2, 113.8, 114.3 (2C), 118.6, 122.7, 123.0, 125.5, 126.2, 126.8, 129.0, 130.2 (2C), 131.5, 133.5, 134.6, 162.4, 164.3, 171.2. Anal. Calcd (found) for $C_{22}H_{19}NO_4$: C, 73.12 (73.23); H, 5.30 (5.23); N, 3.88% (3.56%).

4.4.13. *cis*-2-(4-Cyanophenyl)-4-methoxycarbonyl-5-(1-naphthyl)-4,5-dihydrooxazole (*cis*-2f). Mp 172.0–173.0 °C. IR (KBr): 2229, 1745, 1650 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.72 (3H, s), 5.69 (1H, d, J=10.3 Hz), 6.94 (1H, d, J=10.3 Hz), 7.41 (1H, dd, J=7.4, 7.4 Hz), 7.46 (1H, d, J=7.4 Hz), 7.59 (1H, dd, J=8.6, 8.6 Hz), 7.61 (1H, dd, J=8.6, 8.6 Hz), 7.81 (1H, d, J=7.4 Hz), 8.07 (2H, d, J=8.0 Hz), 8.09 (1H, d, J=8.6 Hz), 8.15 (1H, d, J=8.6 Hz), 8.23 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 51.3, 73.2, 81.0, 115.0, 118.6, 123.4, 123.9, 125.5, 126.3, 126.7, 128.8, 129.0, 129.4 (2C), 130.0, 131.1, 132.0, 133.2, 133.4 (2C), 164.5, 169.1. Anal. Calcd (found) for $C_{22}H_{16}N_2O_3$: C, 74.15 (74.35); H, 4.53 (4.46); N, 7.86% (7.93%).

4.4.14. *trans*-2-(4-Cyanophenyl)-4-methoxycarbonyl-5-(1-naphthyl)-4,5-dihydrooxazole (*trans*-2f). Mp 173.0–174.0 °C. IR (KBr): 2230, 1740, 1639 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.81 (3H, s), 5.00 (1H, d, J=6.9 Hz), 6.77 (1H, d, J=6.9 Hz), 7.52–7.55 (2H, m), 7.61 (1H, dd, J=6.3, 8.2 Hz), 7.64 (1H, dd, J=6.3, 9.2 Hz), 7.97–8.00 (1H, m), 8.01 (1H, d, J=8.2 Hz), 8.04 (1H, d, J=9.2 Hz), 8.04 (2H, d, J=8.2 Hz), 8.19 (2H, d, J=8.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 52.8, 75.1, 81.0, 114.6, 118.1, 122.7, 123.3, 125.5, 126.2, 126.9, 128.98, 129.00 (2C), 129.2, 129.4, 130.4, 133.0 (2C), 133.5, 133.9, 163.3, 170.6. Anal. Calcd (found) for $C_{22}H_{16}N_2O_3$: C, 74.15 (73.83); H, 4.53 (4.16); N, 7.86% (7.77%).

4.4.15. *cis*-2,5-Diphenyl-4-methoxycarbonyl-4,5-dihydrooxazole (*cis*-2g). Mp 141.0–142.0 °C. IR (KBr): 1748, 1649 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.12 (3H, s), 5.38 (1H, d, J=10.3 Hz), 6.13 (1H, d, J=10.3 Hz), 7.25 (2H, d, J=6.9 Hz), 7.33 (1H, dd, J=7.4, 7.4 Hz), 7.37 (2H, dd, J=6.9, 7.4 Hz), 7.56 (2H, dd, J=7.4, 7.4 Hz), 7.65 (1H, dd, J=7.4, 7.4 Hz), 8.00 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 51.2, 73.2, 82.1, 126.1 (2C), 126.6, 128.1 (2C), 128.2 (2C), 128.4, 128.8 (2C), 132.2, 136.1, 165.0, 169.2. Anal. Calcd (found) for $C_{17}H_{15}NO_3$: C, 72.58 (72.52); H, 5.37 (5.46); N, 4.98% (4.89%).

4.4.16. *trans*-2,5-Diphenyl-4-methoxycarbonyl-4,5-dihydrooxazole (*trans*-2g). Oily liquid. IR (NaCl): 1744, 1631 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.76 (3H, s), 4.83 (1H, d, J=7.4 Hz), 5.29 (1H, d, J=7.4 Hz), 7.40 (2H, d, J=6.9 Hz), 7.39 (1H, dd, J=6.9, 6.9 Hz), 7.44 (2H, dd, J=6.9, 6.9 Hz), 7.54 (2H, dd, J=7.4, 7.4 Hz), 7.63 (1H, dd, J=7.4, 7.4 Hz), 7.98 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 52.5, 75.8, 82.7, 125.8 (2C), 126.4, 128.2 (2C), 128.7, 128.8 (2C), 128.9 (2C), 132.3, 139.4, 164.2, 170.8. Anal. Calcd (found) for $C_{17}H_{15}NO_3$: C, 72.58 (72.46); H, 5.37 (5.35); N, 4.98% (4.92%).

4.4.17. *cis*-4-*tert*-Butoxycarbonyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2h). Mp 96.0–97.0 °C. IR (KBr): 1736, 1655 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.99 (9H, s), 3.73 (3H, s), 5.18 (1H, d, J=10.9 Hz), 6.02 (1H, d, J=10.9 Hz), 6.93 (2H, d, J=8.6 Hz), 7.20 (2H, d, J=8.6 Hz), 7.54 (2H, dd, J=7.4, 8.0 Hz), 7.62 (1H, dd, J=7.4, 7.4 Hz), 7.96 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.0 (3C), 55.2, 73.1, 80.4, 82.0, 113.6 (2C), 126.9, 128.1 (2C), 128.2 (2C), 128.8 (2C), 131.6, 132.1, 159.4, 164.5, 167.8. Anal. Calcd (found) for $C_{21}H_{23}NO_4$: C, 71.37 (71.29); H, 6.56 (6.42); N, 3.96% (3.77%).

4.4.18. *trans*-4-*tert*-Butoxycarbonyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2h). Mp 105.0–106.0 °C. IR (KBr): 1726, 1638 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.46 (9H, s), 3.76 (3H, s), 4.66 (1H, d, J=7.4 Hz), 5.74 (1H, d, J=7.4 Hz), 6.98 (2H, d, J=8.6 Hz), 7.33 (2H, d, J=8.6 Hz), 7.52 (2H, dd, J=7.4, 8.0 Hz), 7.61 (1H, dd, J=7.4, 7.4 Hz), 7.95 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 55.2, 76.6, 81.6, 83.0, 114.3 (2C), 126.7, 127.6 (2C), 128.1 (2C), 128.8 (2C), 131.4, 132.1, 159.5, 163.9, 169.6. Anal. Calcd (found) for $C_{21}H_{23}NO_4$: C, 71.37 (70.97); H, 6.56 (6.47); N, 3.96% (3.82%).

4.4.19. *cis*-4-*tert*-Butoxycarbonyl-2-phenyl-5-(4-methylphenyl)-4,5-dihydrooxazole (*cis*-2i). Mp 97.0–98.0 °C. IR (KBr): 1740, 1659 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.96 (9H, s), 2.28 (3H, s), 5.20 (1H, d, J=10.9 Hz), 6.02 (1H, d, J=10.9 Hz), 7.15–7.19 (4H, m), 7.54 (2H, dd, J=7.4, 8.0 Hz), 7.63 (1H, dd, J=7.4, 7.4 Hz), 7.97 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.7, 26.9 (3C), 73.1, 80.4, 82.2, 126.7 (2C), 126.8, 128.1 (2C), 128.6 (2C), 128.8 (2C), 132.1, 133.5, 137.7, 164.5, 167.7. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.70); H, 6.87 (6.71); N, 4.15% (4.12%).

4.4.20. *trans*-4-*tert*-Butoxycarbonyl-2-phenyl-5-(4-methylphenyl)-4,5-dihydrooxazole (*trans*-2i). Mp 98.0–99.0 °C. IR (KBr): 1728, 1636 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.45 (9H, s), 2.30 (3H, s), 4.62 (1H, d, J=7.4 Hz), 5.74 (1H, d, J=7.4 Hz), 7.22–7.27 (4H, m), 7.52 (2H, dd, J=7.4, 8.0 Hz), 7.61 (1H, dd, J=7.4, 7.4 Hz), 7.94 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6, 30.7 (3C), 76.7, 81.6, 83.0, 125.8 (2C), 126.6, 128.2 (2C), 128.8 (2C), 129.4 (2C), 132.2, 136.6, 138.1, 164.0, 169.5. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.41); H, 6.87 (6.62); N, 4.15% (4.70%).

4.4.21. *cis*-4-*tert*-Butoxycarbonyl-2,5-diphenyl-4,5-dihydrooxazole (*cis*-2j). Mp 108.0–109.0 °C. IR (KBr): 1748, 1653 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.95 (9H, s), 5.22 (1H, d, J=10.9 Hz), 6.06 (1H, d, J=10.9 Hz), 7.29 (2H, d, J=6.9 Hz), 7.33 (1H, dd, J=6.9, 6.9 Hz), 7.38 (2H, dd, J=6.9, 6.9 Hz), 7.54 (2H, dd, J=7.4, 7.4 Hz), 7.63 (1H, dd, J=7.4, 7.4 Hz), 7.98 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.9 (3C), 73.1, 80.4, 82.2, 126.7 (2C), 126.8, 128.07 (2C), 128.10 (2C), 128.3, 128.8 (2C), 132.1, 136.5, 164.6, 167.6. Anal. Calcd (found) for $C_{20}H_{21}NO_3$: C, 74.28 (73.94); H, 6.55 (6.21); N, 4.33% (4.39%).

4.4.22. *trans*-4-*tert*-Butoxycarbonyl-2,5-diphenyl-4,5-dihydrooxazole (*trans*-2j). Mp 89.0–90.0 °C. IR (KBr): 1734, 1643 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.47 (9H, s), 4.66 (1H, d, J=7.4 Hz), 5.88 (1H, d, J=7.4 Hz), 7.38–7.40 (3H, m), 7.44 (2H, dd, J=6.9, 7.6 Hz), 7.53 (2H, dd, J=7.4, 7.4 Hz), 7.62 (1H, dd, J=7.4, 7.4 Hz), 7.97 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 76.8, 81.7, 82.9, 125.7 (2C), 126.5, 128.2 (2C), 128.6, 128.8 (2C), 128.9 (2C), 132.2, 139.6, 164.0, 169.4. Anal. Calcd (found) for $C_{20}H_{21}NO_3$: C, 74.28 (74.23); H, 6.55 (6.25); N, 4.33% (4.46%).

4.4.23. *cis*-4-*tert*-Butoxycarbonyl-5-(4-chlorophenyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2k). Mp 100.0–101.0 °C. IR (KBr): 1746, 1643 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.00 (9H, s), 5.22 (1H, d, J=10.9 Hz), 6.09 (1H, d, J=10.9 Hz), 7.32 (2H, d, J=8.6 Hz), 7.46 (2H, d, J=8.6 Hz), 7.55 (2H, dd, J=7.4, 7.4 Hz), 7.63 (1H, dd, J=7.4, 7.4 Hz), 7.98 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.8 (3C), 74.0, 81.5, 82.3, 127.5, 128.9 (2C), 129.0 (2C), 129.5 (2C), 129.6 (2C), 133.0, 133.8, 136.3, 165.4, 168.4. Anal. Calcd (found) for $C_{20}H_{20}ClNO_3$: C, 67.13 (66.99); H, 5.63 (5.30); N, 3.91% (3.96%).

4.4.24. *trans*-4-*tert*-Butoxycarbonyl-5-(4-chlorophenyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2k). Mp 88.0–89.0 °C. IR (KBr): 1732, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.47 (9H, s), 4.68 (1H, d, J=7.4 Hz), 5.84 (1H, d, J=7.4 Hz), 7.42 (2H, d, J=8.6 Hz), 7.50 (2H, d, J=8.6 Hz), 7.54 (2H, dd, J=7.4, 8.0 Hz), 7.63 (1H, dd, J=8.0, 8.0 Hz), 7.97 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.2 (3C), 76.3, 81.4, 81.7, 126.0, 127.3 (2C), 127.8 (2C), 128.4 (2C), 128.5 (2C), 131.8, 132.8, 138.1, 163.5, 168.9. Anal. Calcd (found) for $C_{20}H_{20}ClNO_3$: C, 67.13 (67.12); H, 5.63 (5.38); N, 3.91% (3.92%).

4.4.25. *cis*-4-*tert*-Butoxycarbonyl-5-(4-cyanophenyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2l). Mp 158.0–159.0 °C. IR (KBr): 2226, 1742, 1647 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.98 (9H, s), 5.28 (1H, d, J=10.9 Hz), 6.19 (1H, d, J=10.9 Hz), 7.52 (2H, d, J=8.0 Hz), 7.55 (2H, dd, J=7.4, 8.6 Hz), 7.65 (1H, dd, J=7.4, 7.4 Hz), 7.89 (2H, d, J=8.6 Hz), 7.99 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.9 (3C), 73.2, 80.9, 81.3, 111.0, 118.6, 126.4, 127.7 (2C), 128.2 (2C), 128.9 (2C), 132.2 (2C), 132.3, 141.9, 164.6, 167.4. Anal. Calcd (found) for $C_{21}H_{20}N_2O_3$: C, 72.40 (72.75); H, 5.79 (5.80); N, 8.04% (7.99%).

4.4.26. *trans*-4-*tert*-Butoxycarbonyl-5-(4-cyanophenyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2l). Oily liquid. IR (NaCl): 2230, 1724, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.48 (9H, s), 4.71 (1H, d, J=7.4 Hz), 5.95 (1H, d, J=7.4 Hz), 7.55 (2H, dd, J=7.5, 7.5 Hz), 7.59 (2H, d, J=8.6 Hz), 7.64 (1H, dd, J=7.4, 7.4 Hz), 7.92 (2H, d, J=8.6 Hz), 7.99 (2H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 76.6, 81.85, 81.94, 111.3, 118.5, 126.3, 126.6 (2C), 128.2 (2C), 128.9 (2C), 132.9 (2C), 132.4, 144.9, 163.5, 168.9. Anal. Calcd (found) for $C_{21}H_{20}N_2O_3$: C, 72.40 (72.38); H, 5.79 (5.70); N, 8.04% (7.97%).

4.4.27. *cis*-4-*tert*-Butoxycarbonyl-2-phenyl-5-(2-methylphenyl)-4,5-dihydrooxazole (*cis*-2m). Oily liquid. IR (NaCl): 1744, 1649 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-

d_6): δ 0.92 (9H, s), 2.37 (3H, s), 5.24 (1H, d, J=11.0 Hz), 6.20 (1H, d, J=11.0 Hz), 7.17–7.25 (4H, m), 7.56 (2H, dd, J=6.9, 7.6 Hz), 7.64 (1H, dd, J=6.9, 6.9 Hz), 8.00 (2H, d, J=7.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.1, 27.0 (3C), 72.0, 80.4, 80.7, 125.7, 125.9 (2C), 127.0, 128.2, 128.3 (2C), 129.0, 130.1, 132.3, 134.9, 135.5, 164.9, 167.9. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (74.70); H, 6.87 (6.82); N, 4.15% (4.03%).

4.4.28. *trans*-4-*tert*-Butoxycarbonyl-2-phenyl-5-(2-methylphenyl)-4,5-dihydrooxazole (*trans*-2m). Oily liquid. IR (NaCl): 1734, 1641 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.47 (9H, s), 2.33 (3H, s), 4.54 (1H, d, J=6.9 Hz), 6.03 (1H, d, J=6.9 Hz), 7.18 (1H, d, J=7.6 Hz), 7.21–7.27 (3H, m), 7.55 (2H, dd, J=7.6, 7.6 Hz), 7.64 (1H, dd, J=7.6, 7.6 Hz), 8.00 (2H, d, J=7.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 18.6, 27.6 (3C), 76.3, 80.8, 81.9, 124.8, 126.38, 126.41, 128.2 (2C), 128.3, 128.9 (2C), 130.8, 132.3, 134.5, 137.5, 164.3, 169.7. Anal. Calcd (found) for $C_{21}H_{23}NO_3$: C, 74.75 (75.11); H, 6.87 (6.87); N, 4.15% (4.17%).

4.4.29. *cis*-4-*tert*-Butoxycarbonyl-2-phenyl-5-(2,6-dimethylphenyl)-4,5-dihydrooxazole (*cis*-2n). Oily liquid. IR (NaCl): 1734, 1655 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.98 (9H, s), 5.28 (1H, d, J=10.9 Hz), 6.19 (1H, d, J=10.9 Hz), 7.52 (2H, d, J=8.0 Hz), 7.55 (2H, dd, J=7.4, 8.6 Hz), 7.65 (1H, dd, J=7.4, 7.4 Hz), 7.89 (2H, d, J=8.6 Hz), 7.99 (2H, d, J=8.0 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.4, 26.7 (3C), 72.0, 80.2, 80.4 (2C), 126.9 (2C), 127.9 (2C), 128.0 (2C), 128.9 (2C), 130.1, 132.1, 136.6, 136.9, 164.1, 168.2. Anal. Calcd (found) for $C_{22}H_{25}NO_3$: C, 75.19 (75.33); H, 7.15 (7.32); N, 3.99% (3.89%).

4.4.30. *cis*-4-*tert*-Butoxycarbonyl-5-(2-naphthyl)-2-phenyl-4,5-dihydrooxazole (*cis*-2o). Mp 142.0–143.0 °C. IR (KBr): 1736, 1655 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.77 (9H, s), 5.29 (1H, d, J=11.0 Hz), 6.24 (1H, d, J=11.0 Hz), 7.38 (1H, d, J=8.2 Hz), 7.50–7.53 (2H, m), 7.55 (2H, dd, J=7.6, 7.6 Hz), 7.64 (1H, dd, J=7.6, 7.6 Hz), 7.87 (1H, s), 7.89–7.93 (3H, m), 8.02 (2H, d, J=7.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.8 (3C), 73.3, 80.4, 82.4, 124.4, 125.7, 126.3, 126.5, 126.8, 127.5, 127.7, 127.8, 128.2 (2C), 128.8 (2C), 132.1, 132.4, 132.8, 133.9, 164.7, 167.7. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (76.83); H, 6.21 (6.40); N, 3.75% (3.76%).

4.4.31. *trans*-4-*tert*-Butoxycarbonyl-5-(2-naphthyl)-2-phenyl-4,5-dihydrooxazole (*trans*-2o). Mp 103.0–104.0 °C. IR (KBr): 1730, 1638 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.47 (9H, s), 4.77 (1H, d, J=7.6 Hz), 5.97 (1H, d, J=7.6 Hz), 7.47 (1H, d, J=8.2 Hz), 7.52–7.55 (4H, m), 7.62 (1H, dd, J=7.6, 7.6 Hz), 7.92–8.01 (6H, m). ^{13}C NMR (125 MHz, DMSO-d_6): δ 27.6 (3C), 76.7, 81.7, 83.2, 123.3, 125.0, 126.57 (2C), 126.64, 127.6, 128.0, 128.2 (2C), 128.8 (2C), 128.9, 132.2, 132.6, 132.8, 136.8, 164.0, 169.5. Anal. Calcd (found) for $C_{24}H_{23}NO_3$: C, 77.19 (77.19); H, 6.21 (6.43); N, 3.75% (3.87%).

4.4.32. *cis*-4-*tert*-Butoxycarbonyl-2-*tert*-butyl-5-(1-naphthyl)-4,5-dihydrooxazole (*cis*-2p). Mp 129.0–130.0 °C. IR (KBr): 1726, 1651 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.49 (9H, s), 1.33 (9H, s), 5.18 (1H, d, J=10.3 Hz), 6.52 (1H, d, J=10.3 Hz), 7.42 (1H, d, J=6.9 Hz), 7.50 (1H, dd, J=7.4, 7.4 Hz), 7.52–7.58 (2H, m), 7.87 (1H, d, J=8.0 Hz), 7.94 (1H, d, J=7.4 Hz), 8.02 (1H, d, J=7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.4 (3C), 27.6 (3C), 33.2, 72.1, 79.6, 79.8, 122.9, 127.0, 125.2, 125.8, 126.0, 128.1, 128.3, 130.2, 132.7, 132.9, 167.7, 175.1. Anal. Calcd (found) for $C_{22}H_{27}NO_3$: C, 74.51 (74.46); H, 7.89 (7.70); N, 4.06% (3.96%).

4.4.33. *trans*-4-*tert*-Butoxycarbonyl-2-*tert*-butyl-5-(1-naphthyl)-4,5-dihydrooxazole (*trans*-2p). Any attempts to isolate *trans*-**2p** were unsuccessful owing to its poor yield. The formation of the trans-isomer was deduced from the chemical shift and vicinal coupling constant [δ 4.30 (1H, d, J=6.6 Hz), 6.29 (1H, d, J=6.6 Hz)] of the dihydrooxazole ring-proton signals in DMSO-d_6.

4.4.34. *cis*-5-(9-Anthryl)-4-*tert*-butoxycarbonyl-2-phenyl-4,5-dihydrooxazole (*cis*-2q). Any attempts to isolate *cis*-**2q** were not fruitful owing to its low product composition as well as the difficulty in separating this isomer from (*Z*)-**1q**, (*E*)-**1q**, and certain amounts of by-products. The formation of the cis-isomer was deduced based on the chemical shift and vicinal coupling constant [δ 5.71 (1H, d, J=10.0 Hz)] of the dihydrooxazole ring-proton signals in DMSO-d_6. The other ring-proton signal showed a pronounced overlap with aromatic proton signals, which appeared in the range of 7.2–7.8 ppm.

4.4.35. Methyl 2-benzoylamino-3-(1-naphthyl)propanoate (3a). Mp 110.0–111.0 °C. IR (KBr): 3369, 1757, 1639 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.65 (3H, s), 4.81 (1H, ddd, J=7.6, 8.9, 10.3 Hz), 5.52 (1H, dd, J=8.9, 10.3 Hz), 5.73 (1H, dd, J=10.3, 10.3 Hz), 7.42 (1H, dd, J=7.6, 7.6 Hz), 7.45 (2H, dd, J=7.6, 7.6 Hz), 7.49 (1H, d, J=6.9 Hz), 7.53 (1H, dd, J=5.5, 8.2 Hz), 7.54 (1H, dd, J=5.5, 8.9 Hz), 7.61 (1H, dd, J=6.9, 8.2 Hz), 7.78 (2H, d, J=7.6 Hz), 7.81 (1H, d, J=8.2 Hz), 7.94 (1H, d, J=8.2 Hz), 8.16 (1H, d, J=8.9 Hz), 8.96 (1H, d, J=7.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 34.0, 52.5, 53.9, 123.6, 125.8, 126.1, 126.8, 127.72, 127.75 (2C), 127.8, 128.7 (2C), 129.2, 131.8, 131.9, 133.8, 133.96, 133.97, 166.9, 172.6.

4.5. Control experiment

In order to investigate whether the concentration of TEA is changed during irradiation, an NMR tube was employed instead of a Pyrex vessel. A CD_3OD solution of (*Z*)-**1a** (0.025 mol dm^{-3}, 1 mL) containing TEA (0.10 mol dm^{-3}) and 1,4-dioxane (0.10 mol dm^{-3}) was placed in an NMR tube, which was sealed after the solution was saturated with nitrogen. This CD_3OD solution was irradiated for 4–8 h at room temperature with Pyrex-filtered light from a 450 W high-pressure Hg lamp mounted in a homemade lamp house and subjected to ^{1}H NMR spectral analysis.

4.6. X-ray crystallographic analysis of *cis*-2a and *trans*-2a

A colorless crystal (of the molecular formula $C_{21}H_{17}NO_3$) having approximate dimensions of 0.35×0.23×0.20 mm (*cis*-**2a**) or 0.18×0.18×0.10 mm (*trans*-**2a**) was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ=0.71069 Å) on a Rigaku RAXIS-RAPID equipped with an imaging plate. Data collection and cell refinement: MSC/AFC diffractometer control. Data reduction: teXsan for windows version 1.06.[15] Structure solution: SIR92.[16] Refinement: SHELXL97.[17]

Crystal data for *cis*-**2a**. $C_{21}H_{17}NO_3$, fw=331.36; colorless prism, space group $P2_1/c$; a=8.2216(4) Å, b=18.288(1) Å, c=10.9309(7) Å, α=90.00°, β=94.889(3)°, γ=90.00°, V=1637.55(18) Å^3; Z=4; D_{calcd}=1.344 g cm^{-3}; R=0.0468, $wR(F^2)$=0.1573.

Crystal data for *trans*-**2a**. $C_{21}H_{17}NO_3$, fw=331.36; colorless prism, space group $P1$; a=9.031(8) Å, b=9.133(8) Å, c=10.526(9) Å, α=86.57(5)°, β=80.10(5)°, γ=75.19(5)°, V=826(1) Å^3; Z=2; D_{calcd}=1.33 g cm^{-3}; R=0.153, $wR(F^2)$= 0.464.

Crystallographic data (excluding these structure factors) for *cis*-**2a** and *trans*-**2a** described in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 228004 and CCDC 264885, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References and notes

1. (a) Mariano, P. S.; Stavinoha, J. L. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, NY, 1984; pp 145–257; (b) Oelgemöller, M.; Bunte, J. O.; Mattay, J. *Synthetic Organic Photochemistry*; Griesbeck, A. G., Mattay, J., Eds.; Marcel Dekker: New York, NY, 2005; pp 269–297.
2. (a) Lewis, F. D.; Bassani, D. M.; Reddy, G. D. *J. Org. Chem.* **1993**, *58*, 6390–6393; (b) Lewis, F. D.; Reddy, G. D.; Bassani, D. M.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1994**, *116*, 597–605; (c) Lewis, F. D.; Bassani, D. M.; Burch, E. L.; Cohen, B. E.; Engleman, J. A.; Reddy, G. D.; Schneider, S.; Jaeger, W.; Gedeck, P.; Gahr, M. *J. Am. Chem. Soc.* **1995**, *117*, 660–669.
3. Hoshina, H.; Kubo, K.; Morita, A.; Sakurai, T. *Tetrahedron* **2000**, *56*, 2941–2951.
4. Hoshina, H.; Tsuru, H.; Kubo, K.; Igarashi, T.; Sakurai, T. *Heterocycles* **2000**, *53*, 2261–2274.
5. (a) Kubo, K.; Ishii, Y.; Sakurai, T.; Makino, M. *Tetrahedron Lett.* **1998**, *39*, 4083–4086; (b) Maekawa, K.; Igarashi, T.; Kubo, K.; Sakurai, T. *Tetrahedron* **2001**, *57*, 5515–5526; (c) Motohashi, T.; Maekawa, K.; Kubo, K.; Igarashi, T.; Sakurai, T. *Heterocycles* **2002**, *57*, 269–292.
6. (a) Overman, L. E.; Tsuboi, S.; Angle, S. *J. Org. Chem.* **1979**, *44*, 2323–2325; (b) Burger, K.; Huber, E.; Schöntag, W.; Ottlinger, R. *J. Chem. Soc., Chem. Commun.* **1983**, 945–947; (c) Ibarra, C. A.; Cereceda, J. A.; Ortiz, P.; Vicente, A.; Quiroga, M. L. *Tetrahedron Lett.* **1985**, *26*, 243–246; (d) Roberto, D.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1987**, 212–213; (e) Minozzi, F.; Venturello, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1255–1256; (f) Hassner, A.; Amarasekara, A. S.; Andisik, D. *J. Org. Chem.* **1988**, *53*, 27–30; (g) Wipf, P.; Miller, C. P. *Tetrahedron Lett.* **1992**, *33*, 907–910; (h) Einsiedel, J.; Schoerner, C.; Gmeiner, P. *Tetrahedron* **2003**, *59*, 3403–3407.
7. Einsiedel, J.; Hübner, H.; Gmeiner, P. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2533–2536.
8. (a) Rao, Y. S.; Filler, R. *Synthesis* **1975**, 749–764; (b) Rzeszotarska, B.; Karolak-Wojciechowska, J.; Broda, M. A.; Galdecki, Z.; Trzezwinska, B.; Koziol, A. E. *Int. J. Pept. Protein Res.* **1994**, *44*, 313–319.
9. Cambridge Crystallographic Data Centre, Mercury 1.2: Crystal structure visualization and exploration made easy, 12 Union Road, Cambridge CB2 1EZ, UK, 2004.
10. MM2 and PM5 calculations were accomplished by using CAChe 5.0 for Windows available from Fujitsu Ltd, 2002.
11. (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271; (b) Rehm, D.; Weller, A. *Z. Phys. Chem.* **1970**, *69*, 183–200.
12. Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991; 256–263.
13. Sasaki, Y.; Maekawa, K.; Watanabe, H.; Matsumoto, T.; Kubo, K.; Igarashi, T.; Sakurai, T. *Tetrahedron Lett.* **2007**, *48*, 4765–4770.
14. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: Chichester, UK, 1986.
15. Molecular Structure Corporation. *teXan for Windows. Single Crystal Structure Analysis Software, Ver. 1.06*; The Woodlands: Texas, 1999.
16. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 1045–1050.
17. Sheldrick, G. M. *SHELXL 97. Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, 1997.