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SYNTHESIS AND PHOTOCHEMICAL PROPERTIES OF 2,4,6,-TRIARYL-4*H*-1,4-OXAZINES

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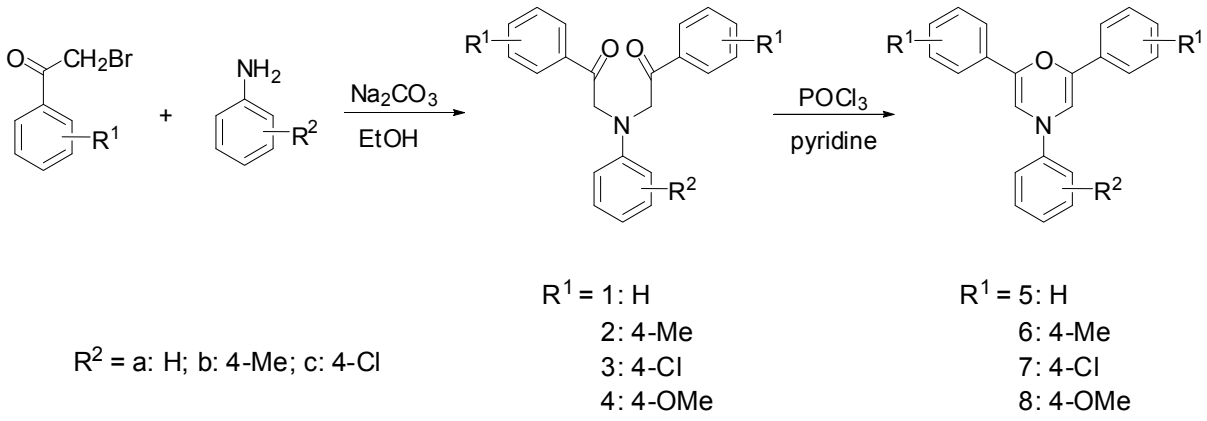
Abstract – A series of 2,4,6-triaryl-4*H*-1,4-oxazines was synthesized, and their photochemical properties were studied. The 2,4,6-triaryl-4*H*-1,4-oxazines underwent photoreaction to *N*-(1-methoxy-2-oxo-2-arylethyl)-*N*-arylformamides determined by ^{1}H NMR, ^{13}C NMR, MS, and single crystal X-ray diffraction analyses.

INTRODUCTION

Heterocycles possess intrinsic reactivity that enables a wide variety of versatile and productive transformations. Because of their ubiquitous presence in natural products and drugs, the development of novel and efficient preparations of these structures remains a fundamental goal of organic synthesis. Although the importance of 1,4-oxazines has been extensively documented, primarily as a result of pharmaceutical and chromogenic research,[1-8] there is only one known synthesis of 2,4,6-triphenyl-4*H*-1,4-oxazine.[9] In connection with our research on the synthesis of heterocycles containing nitrogen or oxygenand particular interest in six-membered rings,[10-12] we intended to prepare a series of oxazines and broaden the scope of the reported method. A series of the desired 2,4,6-triaryl-4*H*-1,4-oxazines was synthesized by the reaction of *N*,*N*-bis(phenacyl)anilines with an excess of $POCl_3$ in pyridine (Scheme 1). Because we are interested in the photochemical properties of heterocycles containing nitrogen or oxygen,[13-16] the photochemical properties of the triaryl-4*H*-1,4-oxazines were investigated. The 2,4,6-triaryl-4*H*-1,4-oxazine was unstable and photoreacted to the *N*-(1-methoxy-2-oxo-2-arylethyl)-*N*-arylformamide during UV irradiation in MeOH (Scheme 2).

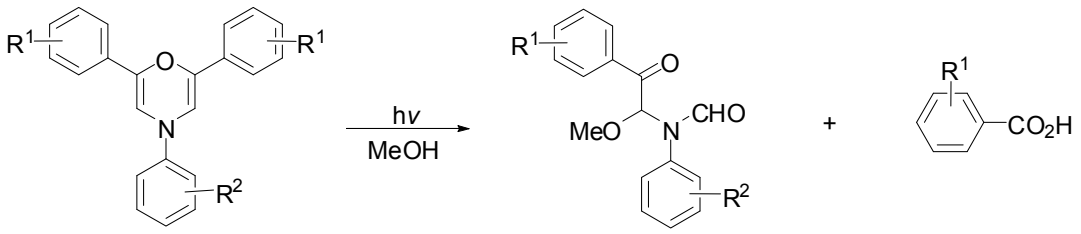


R^1 = 1: H
2: 4-Me
3: 4-Cl
4: 4-OMe

R^2 = a: H; b: 4-Me; c: 4-Cl

R^1 = 5: H
6: 4-Me
7: 4-Cl
8: 4-OMe

Scheme 1. Synthesis of 2,4,6-triaryl-4*H*-1,4-oxazines



5a, 5b and 7a

9a: R^1 = R^2= H
9b: R^1 = H, R^2 = 4-Me
10a: R^1 = 4-Cl, R^2 = H

11: R^1 = H
12: R^1 = 4-Cl

Scheme 2. Photoreaction of 2,4,6-triaryl-4*H*-1,4-oxazines

RESULTS AND DISCUSSION

Synthesis of 2,4,6-triaryl-4*H*-1,4-oxazines (5-8)

The synthesis of the 2,4,6-triaryl-4*H*-1,4-oxazines was carried out according to the literature,[9] and 2,4,6-triphenyl-4*H*-1,4-oxazine (**5a**) was obtained as the only product by the reaction of *N*,*N*-bis(phenacyl)aniline (**1a**) with an excess of $POCl_3$ in pyridine. When substituents (R^1 and R^2) were introduced on the phenyl rings, the breadth of the method was shown by the formation of various 4*H*-1,4-oxazines (Table 1). The yields of the triaryl-4*H*-1,4-oxazines varied predictably with the identity of the substituents (R^1 and R^2), and the best yields of **7c** were obtained when R^1 and R^2 were both 4-Cl (74%). For example, when R^1 is H, the yield of **5c** (R^2 = 4-Cl) is higher than that of **5a** and **5b**. When R^2 is H, the yield of **7a** (R^1 = 4-Cl) was higher than that of **5a** or **6a**. These results show that an electron-withdrawing group at R^1 and R^2 is preferred. It is probably because the electron-withdrawing group is beneficial for the large conjugated structure and decreases the electronic density throughout. When R^1 is 4-OMe, a trace of **8a-c** was observed by TLC during the reaction and disappeared within a

few minutes. The phenyl rings with strong electron-donating groups (R^1 = 4-OMe) may cause the 2,4,6-triaryl-4*H*-1,4-oxazines to be unstable.

Table 1. The yields of 2,4,6-triaryl-4*H*-1,4-oxazines (**5-8**)

Products	R^1	R^2	Yields[a](%)
5a	H	H	50
5b	H	4-Me	53
5c	H	4-Cl	63
6a	4-Me	H	53
6b	4-Me	4-Me	57
6c	4-Me	4-Cl	63
7a	4-Cl	H	60
7b	4-Cl	4-Me	65
7c	4-Cl	4-Cl	74
8a	4-OMe	H	-
8b	4-OMe	4-Me	-
8c	4-OMe	4-Cl	-

[a] Isolated yields.

Photochemical study of 2,4,6-triaryl-4*H*-1,4-oxazines (5-8)

In this experiment, the 2,4,6-triaryl-4*H*-1,4-oxazines were found to be stable in the solid state and unstable in solution. Due to their common features, **5a** was chosen as a representative compound to investigate their stability in a variety of conventional solvents (such as MeOH, benzene, hexane, dichloromethane, EtOAc, acetone, tetrahydrofuran, acetonitrile, pyridine, and so on). The results showed that **5a** was unstable in solvents, except for MeOH, acetone and pyridine. And **5a** was found more soluble in MeOH than acetone and pyridine. So, MeOH was chosen as the solvent in the study of the photochemical properties of the title compounds.

Table 2. The UV-Vis absorption data of 2,4,6-triaryl-4*H*-1,4-oxazines (**5a-c**) and (**7a-c**)

Compounds	**5a**	**5b**	**5c**	**7a**	**7b**	**7c**
λ_{max}(nm)	236	236	240	244	242	244
	346	348	346	354	354	352
	436	444	438	454	456	450
ε_{max}($Lmol^{-1}cm^{-1}$)	20,981	41,407	51,333	21,459	27,000	29,563
	22,941	45,519	50,481	18,152	23,389	26,169
	3,278	7,037	7,574	3,794	4,722	7,369

The UV-Vis absorption spectra of **5** and **7** in MeOH at a concentration of 1×10^{-5} M are shown in Table 2 and Figure 1. Several absorption peaks were observed in the linear absorption spectra for all of the molecules in the wavelength ranging from 220 to 600 nm, while almost no linear absorption was observed beyond 600 nm. The spectral shapes are similar because that these compounds have the same stem nuclei of the 2,4,6-triaryl-4*H*-1,4-oxazine structure. The maximum absorptions range from 236 to 242 nm, 346 to 356 nm, and 436 to 456 nm and are similar to the UV-Vis absorption spectra of **5a**.[9]

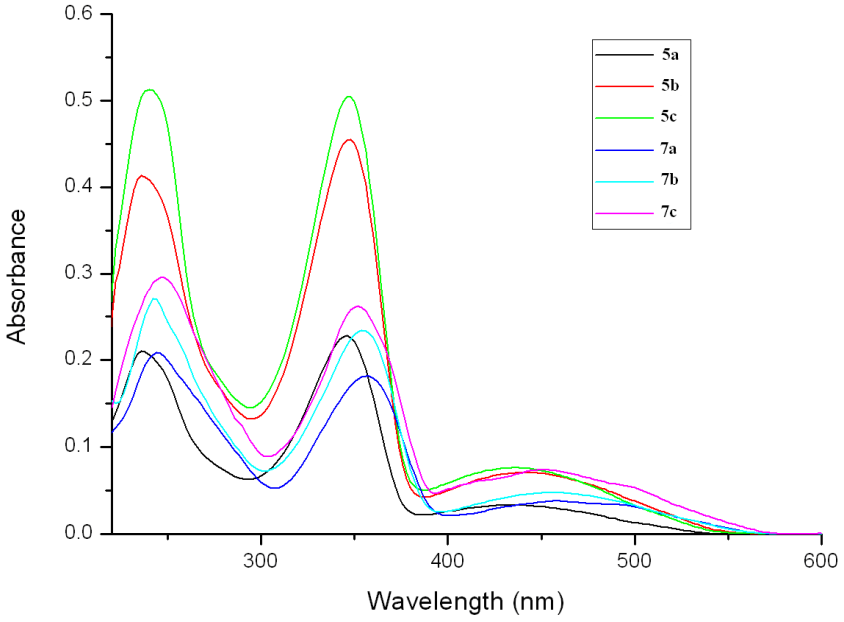


Figure 1. The UV–Vis absorption spectra of **5** and **7** in MeOH at a concentration of 1×10^{-5} M

The results in Table 2 and Figure 1 show that the red shifts of the absorption peaks are observed solely because of the introduction of auxochrome groups on the phenyl ring. For example, when R^1 is the same, the wavelength maximum of **5b** (R^1 = H, R^2 = *p*-Me) is 444 nm, while the wavelength maximum of **7b** (R^1 = *p*-Cl, R^2 = *p*-Me) is 456 nm, which is 12 nm longer than that of **5b**. According to the data above, obviously that when R^1 is auxochrome group, such as -Cl, the UV-Vis absorption spectra of 2,4,6-triaryl-4*H*-1,4-oxazines show red shifts of the absorption peaks.

The photostability was investigated by the changes of UV-Vis absorption spectra irradiated with UV lights of 450 W medium pressure mercury lamp in MeOH at a concentration of 10^{-5} M (Figure2). After irradiation for 1 h, all three wavelength maxima of **5a** and **7a** (236-244 nm, 346-354 nm, and 436-454 nm) decreased dramatically from those taken before the irradiation. In particular, the wavelength maximum at 346-354 nm (the absorbance of the phenyl rings in the 2- and 6-position) decreased in magnitude, and the 436-454 nm peaks (the absorbance of the conjugated ring) disappeared. The changes in the UV-Vis absorption spectra may be caused by fragmenting the conjugated structures during irradiation.

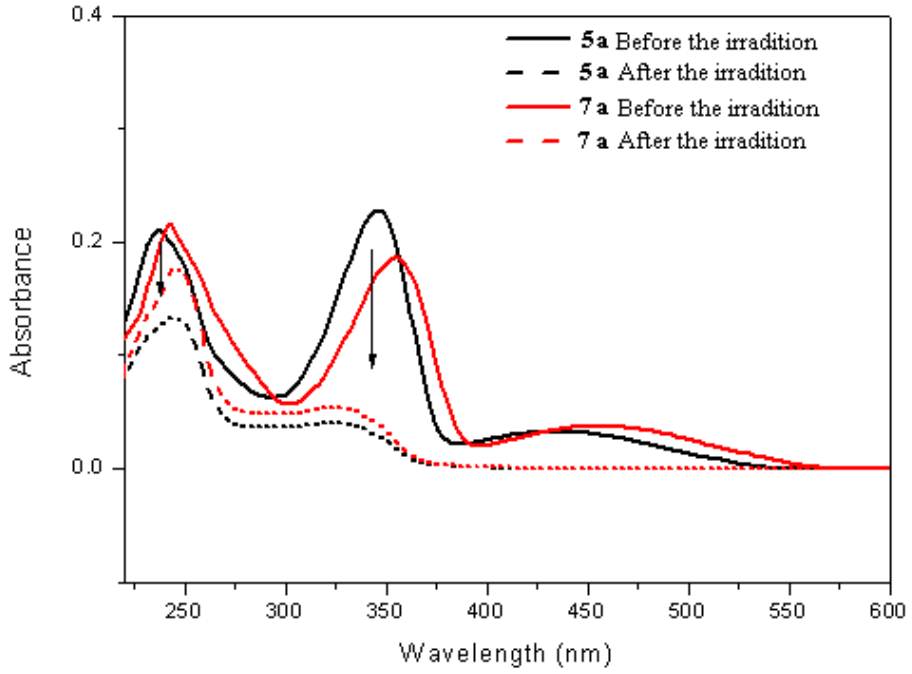


Figure 2. The UV-Vis absorption spectra of **5a** and **7a** before (solid lines) and after (dashed lines) irradiation for 1h in MeOH

To elucidate the photochemical reaction of 2,4,6-triaryl-4*H*-1,4-oxazines, **5a** was used as reactant in a model reaction in MeOH. **5a** was irradiated by a 450 W medium pressure mercury lamp, and the progress

of the reaction was monitored by TLC. After irradiation for approximately 1 h, **9a** and benzoic acid **11** were obtained in the yields of 12% and 10% (Scheme 2). A similar transformation of **5a** also occurred by irradiation with sunlight for about 3 days, and the yields of **9a** and **11** were almost the same as those obtained from irradiation with the mercury lamp. The structure of **9a** was *N*-(1-methoxy-2-oxo-2-phenylethyl)-*N*-phenylformamide confirmed by ^{1}H NMR, ^{13}C NMR, and MS. Due to their structural similarity, compounds **5b** and **7a** were irradiated under the same conditions used for **5a** in MeOH. The results indicate that the 2,4,6-triaryl-4*H*-1,4-oxazines undergo a photoreaction to the *N*-(1-methoxy-2-oxo-2-arylethyl)-*N*-arylformamides (**9**, **10)** and corresponding benzoic acids (**11**, **12**). The substituents on the benzene rings have minor effects on the yields of the photoreaction, e.g., the yields of **9b** and **10a**, which have electron-donating and electron-withdrawing groups, respectively, are similar.

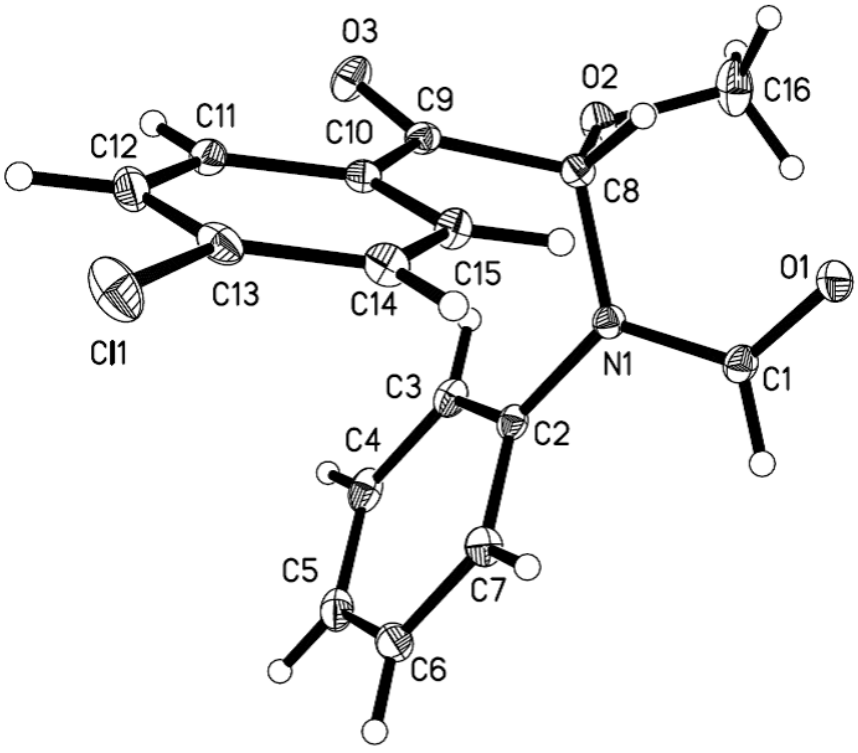
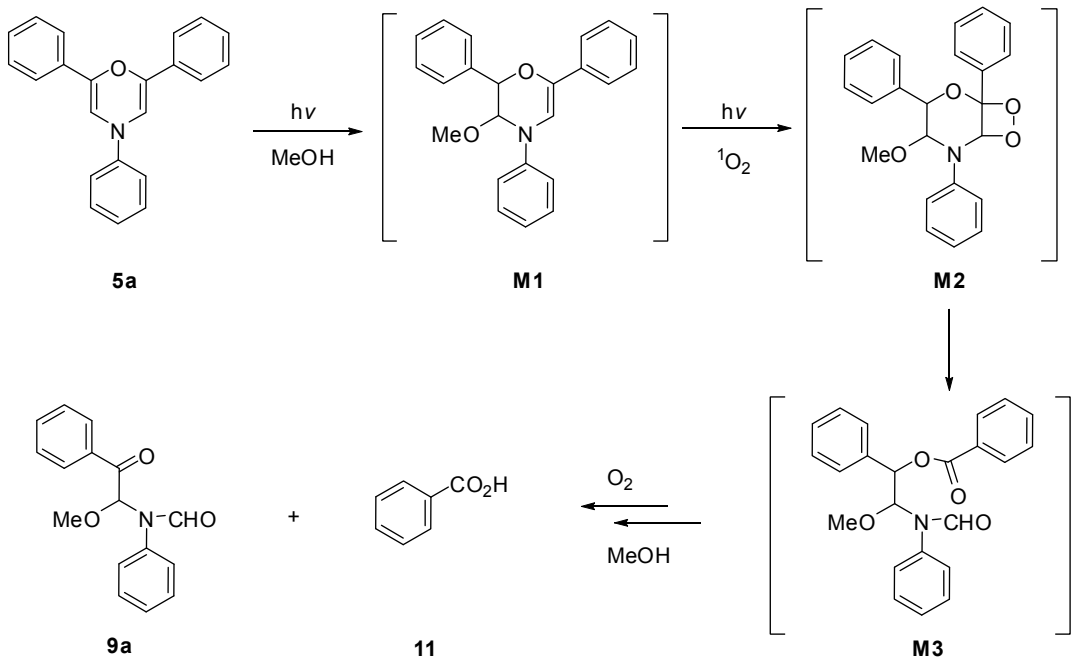


Figure 3. ORTEP diagram of the crystal structure of **10a** (drawn at 50% thermal ellipsoids)

The structures of **9a-b**, **10a** were confirmed by ^{1}H NMR, ^{13}C NMR, and MS. Compound **10a** will be used as a representative example for discussing the details of the structures. In the^{1}H NMR spectra of **10a**, there was a signal from the aldehyde group at δ 8.50, signals corresponding to the 9 protons on the two benzene rings in the range of δ 6.99-7.76, a signal from the methine group at δ 6.92, a signal from the

methoxy groupat δ 3.67. In the ^{13}C NMR spectra of **10a** there were only 12 signals due to the symmetry of the benzene ring. The two carbonyl carbons resided at δ 190.8 and 163.4 respectively, the 8 signals of the benzene rings appeared at δ 82.8-140.4, and the 2 signals from the the two saturated carbons were found at δ 56.6 and 76.7. MS (ESI) *m/z* (%) = 325.7 $[M+Na]^+$. Single crystal X-ray diffraction of **10a** (Deposition number CCDC-735378) further proves that the photoreaction product is *N*-(1-methoxy-2-oxo-2-phenylethyl)-*N*-phenylformamide (Figure 3).



Scheme 3. Supposed mechanism for the formation of **9a**

A mechanism of the formation of **9a** is speculated via the photoaddition by the MeOH and photooxygen by the singlet oxygenshown in Scheme 3. The **5a** is added by MeOH molecule to give **M1** via anti-Markownikoff addition. Actually, when other alcohols were used in this reaction, **5a** could not give the corresponding photoadditional products. The reaction may proceed via photoinduced electron-transfer (PET) between photoexcited **5a** with some kind of electron acceptor (O_2 is possible candidate) to give radical cation of **5a**, then the radical cation of **5a** attacks on MeOH, then deprotonation, one-electron reduction of the resulting radical (maybe from $O_2^{\bullet-}$) to give anion, and protonation, according to Mizuno.[17] The conversion of **M1** to **M2** is speculated to be associated with the singlet oxygen which probably comes from air in solution by absorbing UV (wavelengths <320 nm).[18-22] It was proved by the additions of air and N_2. The formation of **9a** was accelerated with the addition of air and abated under nitrogen atmosphere. The presence of singlet oxygen was proved by the addition of quencher or photosensitizer which can capture the singlet oxygen or convert the oxygen molecule to singlet oxygen.

The quencher was 1,4-diazabicyclo[2.2.2]octane which slowed down the formation of **9a** and **11** dramatically. The photosensitizer was a rubrene which speeded up the reaction considerably. The 1,2-dioxetane **M2** is the precursor of the C-C bond cleavage product **M3** and an intramolecular electron-transfer mechanism is proposed for the cleavage of these peroxides. The **M2** is decomposed by a stepwise process involving homolysis of the peroxide bond to form a diradical with subsequent C-C bond cleavage product **M3**.[23] The *N*-formyl group stabilizes **M3** probably because the electron-withdrawing effect of the formyl prevents the lone-pair electron of the nitrogen from participating in breaking the C-O bond of **M3**.[24] In Scheme 3, there is another possibility that reverses the order of photoaddition of MeOH and singlet oxygen. Namely, route of addition of singlet oxygen occurs first, then MeOH photochemically adds. The accurate and reasonable explanation of the mechanism of the photoreaction of 2,4,6-triaryl-4*H*-1,4-oxazines will be proposed by the further studies.

EXPERIMENTAL

Materials and Methods

All chemicals were purchased from commercial sources and used without further purification. Thin-layer chromatography (TLC) was conducted on silica gel 60 F254 plates (Merck KGaA). Melting points were determined on a XT-5A digital melting point apparatus and are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz using $CDCl_3$ or acetone-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. High-resolution mass spectral (HRMS) analyses were carried out using a VG 70SE mass spectrometer (Manchester, UK), which was operated in electron impact or electrospray ionization mode. UV-Vis absorption spectra were measured using a U-4100 UV/VIS spectrophotometer (Hitachi). Elemental analysis was performed on a vario EL elemental analyzer. Irradiation for both the photostability studies and photochemical reactions was conducted using an Osram HBO 450W/2 medium pressure mercury lamp. To mimic UV radiation, a 10-mm-thick Pyrex filter was placedbetween the lamp and the sample that was irradiated. The filter allows irradiation only by wavelengths greater than 290 nm. The samples were irradiated while in quartz cuvettes.

General procedure for the synthesis of *N*,*N*-bis(phenacyl)anilines

A mixture of phenacyl bromide (12 mmol), Na_2CO_3 (12 mmol), and aniline (6.0 mmol) was stirred under reflux at 110 °C. The progress of the reaction was monitored by TLC. After the indicated reaction time, the solid products **1-4** were recrystallized from EtOH.

***N*,*N*-Bis(phenacyl)aniline (1a).** Yellow needles, yield 65%; mp 196.2-197.4 °C (mp 198 °C[11]); ^{1}H NMR

spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.03 (d, J = 7.2 Hz, 4H, Ar-H), 7.62 (t, J = 7.6 Hz, 2H, Ar-H), 7.51 (t, J = 7.6 Hz, 4H, Ar-H), 7.16 (t, J = 7.6 Hz, 2H, Ar-H), 6.73 (t, J = 7.6 Hz, 1H, Ar-H), 6.55 (d, J = 8.4 Hz, 2H, Ar-H), 4.95 (s, 4H, N-CH_2).

***N,N*-Bis(phenacyl)-4-toluidine (1b).** Yellow needles, yield 73%; mp 153.2-154.1 °C (mp 158 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.01 (d, J = 7.2 Hz, 4H, Ar-H), 7.61 (t, J = 7.6 Hz, 2H, Ar-H), 7.49 (t, J = 7.6 Hz, 4H, Ar-H), 6.75 (d, J = 8.8 Hz, 2H, Ar-H), 6.57 (d, J = 8.8 Hz, 2H, Ar-H), 4.95 (s, 4H, N-CH_2), 2.24 (s, 3H, CH_3).

***N,N*-Bis(phenacyl)-4-chloroaniline (1c).** Yellow needles, yield 55%; mp 158.3-160.2 °C[11]; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.02 (d, J = 7.6 Hz, 4H, Ar-H), 7.67 (t, J = 7.2 Hz, 2H, Ar-H), 7.56 (t, J = 7.6 Hz, 4H, Ar-H), 7.09 (d, J = 8.8 Hz, 2H, Ar-H), 6.50 (d, J = 8.8 Hz, 2H, Ar-H), 5.03 (s, 4H, N-CH_2).

***N,N*-Bis(4-methylphenacyl)aniline (2a).** Yellow needles, yield 62%; mp 103.7-104.5 °C (mp 103 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.93 (d, J = 8.0 Hz, 4H, Ar-H), 7.30 (d, J = 8.0 Hz, 4H, Ar-H), 7.14 (t, J = 7.6 Hz, 2H, Ar-H), 6.73 (d, J = 7.2 Hz, 1H, Ar-H), 6.52 (d, J = 8.4 Hz, 2H, Ar-H), 4.92 (s, 4H, N-CH_2), 2.43 (s, 6H, CH_3).

***N,N*-Bis(4-methylphenacyl)-4-toluidine (2b).** Yellow needles, yield 70%; mp 142.7-144.3 °C (mp 128°C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.91 (d, J = 8.0 Hz, 4H, Ar-H), 7.29 (d, J = 8.0 Hz, 4H, Ar-H), 6.95 (d, J = 8.0, 2H, Ar-H), 6.47 (d, J = 8.4 Hz, 2H, Ar-H), 4.90 (s, 4H, N-CH_2), 2.43 (s, 6H, CH_3), 2.20 (s, 3H, CH_3).

***N,N*-Bis(4-methylphenacyl)-4-chloroaniline (2c).** Yellow needles, yield 54%; mp 178.5-179.3 °C[11]; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.90 (d, J = 8.0, 4H, Ar-H), 7.29 (d, J = 8.0 Hz, 4H, Ar-H), 7.08 (d, J = 9.2 Hz, 2H, Ar-H), 6.43 (d, J = 9.2 Hz, 2H, Ar-H), 4.89 (s, 4H, N-CH_2), 2.43 (s, 6H, CH_3).

***N,N*-Bis(4-chlorophenacetyl)aniline (3a).** Yellow needles, yield 76%; mp 108.1-109.8 °C (mp 110 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.96 (d, J = 8.4 Hz, 4H, Ar-H), 7.48 (d, J = 8.4 Hz, 4H, Ar-H), 7.17 (t, J = 8.0 Hz, 2H, Ar-H), 6.76 (t, J = 7.2 Hz, 1H, Ar-H), 6.52 (d, J = 8.0 Hz, 2H, Ar-H), 4.90 (s, 4H, N-CH_2).

***N,N*-Bis(4-chlorophenacyl)-4-toluidine (3b).** Yellow needles, yield 80%; mp 137.3-138.1 °C (mp 140.0 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.93 (d, J = 7.6 Hz, 4H, Ar-H), 7.33 (d, J = 7.6 Hz, 4H, Ar-H), 6.97 (d, J = 8.4 Hz, 2H, Ar-H), 6.49 (d, J = 8.4 Hz, 2H, Ar-H), 4.88 (s, 4H, N-CH_2), 2.23 (s, 3H, CH_3).

***N,N*-Bis(4-chlorophenacyl)-4-chloroaniline (3c).** Yellow needles, yield 67%; mp 181.5-182.3 °C[11]; ^{1}H

NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 7.94 (d, J = 8.4, 4H, Ar-H), 7.49 (d, J = 8.4 Hz, 4H, Ar-H), 7.11 (d, J = 8.4 Hz, 2H, Ar-H), 6.43 (d, J = 8.8 Hz, 2H, Ar-H), 4.87 (s, 4H, N-CH_2).

***N,N*-Bis(4-methoxyphenacyl)aniline (4a).** Yellow needles, yield 60%; mp 150.9-151.2 °C (mp 152.0 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.01 (d, J = 8.8 Hz, 4H, Ar-H), 7.14 (t, J = 8.0 Hz, 2H, Ar-H), 6.97 (d, J = 8.8 Hz, 4H, Ar-H), 6.71 (t, J = 7.6 Hz, 1H, Ar-H), 6.53 (d, J = 8.4 Hz, 2H, Ar-H), 4.89 (s, 4H, N-CH_2), 3.88 (s, 6H, OCH_3).

***N,N*-Bis(4-methoxyphenacyl)-4-toluidine (4b).** Yellow needles, yield 66%; mp 169.2-171.1 °C (mp 170.0 °C[11]); ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.21 (d, J = 8.8 Hz, 4H, Ar-H), 7.96 (d, J = 8.8 Hz, 4H, Ar-H), 6.94 (d, J = 8.0 Hz, 2H, Ar-H), 6.41 (d, J = 8.4 Hz, 2H, Ar-H), 4.80 (s, 4H, N-CH_2), 3.90 (s, 6H, OCH_3), 2.20 (s, 3H, CH_3).

***N,N*-Bis(4-methoxyphenacyl)-4-chloroaniline (4c).** Yellow needles, yield 49%; mp 168.7-169.3 °C[11]; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.06 (d, J = 8.4 Hz, 4H, Ar-H), 7.31 (d, J = 8.4 Hz, 4H, Ar-H), 7.03 (d, J = 8.4 Hz, 2H, Ar-H), 6.50-6.52 (m, 2H, Ar-H), 4.94 (s, 4H, N-CH_2), 3.63 (s, 6H, OCH_3).

General procedure for the synthesis of 2,4,6-triaryl-4*H*-1,4-oxazines

A mixture of *N,N*-bis(phenacyl)anilines (5 mmol) and 0.87 mL (9.4 mmol) of $POCl_3$ in 30 mL of pyridine (dried over CaH_2) was heated with occasional swirling at 100 °C for 45 min. The deep red solution was poured onto 50 mL of crushed ice, and the resulting solid was filtered. The crude products were washed twice with a small amount of MeOH to purify the products.

2,4,6-Triphenyl-4*H*-1,4-oxazine (5a). Orange red powder, yield 50%; mp 181.6-182.4 °C (mp 183.0-185.0 °C[9]); ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.55 (d, J = 6.8 Hz, 4H, Ar-H), 7.29-7.43 (m, 10H, Ar-H), 7.03 (t, J = 6.8 Hz, H, Ar-H), 6.94 (s, 2H, N-CH=); ^{13}C NMR spectra (100 MHz, 25 °C, acetone-d_6): δ 142.3, 138.7, 132.8, 129.7, 128.4, 127.5, 122.8, 120.9, 113.8, 109.3.

2,6-Diphenyl-4-(4-tolyl)-4*H*-1,4-oxazine (5b). Orange red powder, yield 53%; mp 115.7-117.2 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.75 (d, J = 7.6 Hz, 4H, Ar-H), 7.40 (t, J = 7.6 Hz, 4H, Ar-H), 7.29 (t, J = 7.6 Hz, 2H, Ar-H), 7.18 (d, J = 8.4 Hz, 4H, Ar-H), 6.98 (s, 2H, N-CH=), 2.28 (s, 3H, Ar-CH_3); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.0, 137.8, 132.9, 130.0, 129.9, 128.4, 127.1, 122.6, 113.9, 110.0, 19.7; HRMS(ESI): (*m/z*) calcd for $C_{23}H_{19}NO$: 325.1467 $[M]^+$; found 325.1453.

2,6-Diphenyl-4-(4-chlorophenyl)-4*H*-1,4-oxazine (5c). Orange red powder, yield 63%; mp 98.6-99.5 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.77 (d, J = 7.6 Hz, 4H, Ar-H), 7.29-7.43 (m, 10H,

Ar-H), 7.03 (s, 2H, N-CH=); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.7, 138.3, 132.6, 129.2, 128.4, 127.5, 124.6, 122.9, 114.9, 109.0; HRMS(ESI): (*m/z*) calcd for $C_{22}H_{16}ClNO$: 345.0830 $[M]^+$; found 345.0812.

2,6-Bis(4-tolyl)-4-phenyl-4*H*-1,4-oxazine (6a). Orange red powder, yield 53%; mp 113.5-114.2 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.64 (d, J = 7.6 Hz, 4H, Ar-H), 6.92-7.35 (m, 9H, Ar-H), 6.91 (s, 2H, N-CH=), 2.35 (s, 6H, Ar-CH_3); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 142.0, 138.5, 137.0, 130.1, 129.4, 129.0, 122.8, 120.3, 113.4, 108.6, 20.4; HRMS(ESI): (*m/z*) calcd for $C_{24}H_{21}NO$: 339.1623 $[M]^+$; found 339.1602.

2,4,6-Tri(4-tolyl)-4*H*-1,4-oxazine (6b). Orange red powder, yield 57%; mp 133.6-134.2 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.13-7.60 (m, 12H, Ar-H), 6.87 (s, 2H, N-CH=), 2.27 (s, 6H, Ar-CH_3), 2.04 (s, 3H, Ar-CH_3); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.0, 137.8, 132.9, 130.0, 129.9, 128.4, 127.1, 122.6, 113.9, 110.0, 19.7; HRMS(ESI): (*m/z*) calcd for $C_{25}H_{23}NO$: 353.1736 $[M]^+$; found 353.1702.

2,6-Bis(4-tolyl)-4-(4-chlorophenyl)-4*H*-1,4-oxazine (6c). Orange red powder, yield 63%; mp 98.6-99.9 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 6.90-7.47 (m, 12H, Ar-H), 6.44 (s, 2H, N-CH=), 2.38 (s, 6H, Ar-CH_3); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.7, 138.5, 129.4, 129.3, 129.1, 124.2, 122.9, 122.7, 114.7, 109.1, 20.2; HRMS(ESI): (*m/z*) calcd for $C_{24}H_{20}ClNO$: 373.1140 $[M]^+$; found 373.1126.

2,6-Bis(4-chlorophenyl)-4-phenyl-4*H*-1,4-oxazine (7a). Orange red powder, yield 60%; mp 132.5-133.6 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.78 (d, J = 8.0 Hz, 4H, Ar-H), 7.30-7.54 (m, 9H, Ar-H), 7.05 (s, 2H, N-CH=); ^{13}C NMR spectra (100 M Hz, acetone-d_6, 25 °C): δ 140.6, 138.8, 132.6, 129.2, 128.4, 127.5, 124.6, 122.9, 114.9, 109.0; HRMS(ESI): (*m/z*) calcd for $C_{22}H_{15}Cl_2NO$: 379.0531 $[M]^+$; found 379.0516.

2,6-Bis(4-chlorophenyl)-4-(4-tolyl)-4*H*-1,4-oxazine (7b). Orange red powder, yield 65%; mp 153.9-154.7 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.74 (d, J = 8.8 Hz, 4H, Ar-H), 7.39-7.42 (m, 4H, Ar-H), 7.21 (d, J = 8.4 Hz, 2H, Ar-H), 7.16 (d, J = 8.4 Hz, 4H, Ar-H), 6.97 (s, 2H, N-CH=), 2.29 (s, 3H, Ar-CH_3); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.0, 138.8, 132.3, 130.0, 128.4, 128.3, 127.6, 124.5, 113.8, 110.1, 19.6; HRMS(ESI): (*m/z*) calcd for $C_{23}H_{17}C_{l2}NO$: 393.0687 $[M]^+$; found 393.0689.

2,4,6-Tri(4-chlorophenyl-4*H*-1,4-oxazine (7c). Orange red powder, yield 74%; mp 145.3-146.7 °C; ^{1}H NMR spectra (400 MHz, acetone-d_6, 25 °C): δ 7.65 (d, J = 6.8 Hz, 4H, Ar-H), 7.08-7.45 (m, 8H, Ar-H),

6.95 (s, 2H, N-CH=); ^{13}C NMR spectra (100 MHz, acetone-d_6, 25 °C): δ 140.6, 138.7, 132.5, 129.2, 128.2, 127.5, 124.6, 122.8, 114.7, 109.0; HRMS(ESI): (*m/z*) calcd for $C_{22}H_{14}Cl_3NO$: 413.0112 $[M]^+$; found 413.0087.

General procedure for the photoreaction of 2,4,6-triaryl-4*H*-1,4-oxazines

The 2,4,6-triaryl-4*H*-1,4-oxazines (0.32 mmol) were dissolved in MeOH (200 mL) and poured into the photolysis unit. Photo-irradiations were performed using a medium pressure mercury lamp (450 W), and a 10-mm-thick Pyrex filter was placed between the lamp and sample. The reaction was monitored by TLC. After completion, the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel using a mixed solvent of petroleum ether and EtOAc (20:3 v/v) to provide **9**, **10** and the corresponding benzoic acids **11** and **12**.

***N*-(1-Methoxy-2-oxo-2-phenylethyl)-*N*-phenylformamide (9a).** Pale yellow solid, yield 12%; mp 127.2-128.7 °C; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.49 (s, 1H, CHO), 6.98-7.80 (m, 10H, Ar-H), 6.97 (s, 1H, CH), 3.69 (s, 3H, OCH_3); ^{13}C NMR spectra (100 MHz, $CDCl_3$, 25 °C): δ 191.9, 163.5, 137.0, 134.5, 133.8, 129.3, 128.7, 128.2, 128.1, 126.3, 82.8, 56.6; MS(ESI) *m/z* (%) = 291.7 $[M+Na]^+$. Anal. Calcd (%) for $C_{16}H_{15}NO_3$: C 71.36, H 5.61, N 5.20. Found: C 71.35, H 5.58, N 5.22.

***N*-(1-Methoxy-2-oxo-2-phenylethyl)-*N*-(4-tolyl)formamide (9b).** Pale yellow solid, yield 15%; mp 135.5-136.6 °C ; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.47 (s, 1H, CHO), 7.43-7.85 (m, 5H, Ar-H), 7.06 (d, J = 8.0 Hz, 2H, Ar-H), 6.98 (s, 1H, CH), 6.86 (d, J = 8.0 Hz, 2H, Ar-H), 3.69 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR spectra (100 MHz, $CDCl_3$, 25 °C): δ 191.9, 163.5, 138.2, 134.4, 134.3, 133.8, 129.9, 128.7, 128.2, 126.4, 82.7, 56.6, 21.0; MS (ESI) *m/z* (%) = 306.7 $[M+Na]^+$. Anal. Calcd (%) for $C_{17}H_{17}NO_3$: C 72.07, H 6.05, N 4.94. Found: C 72.06, H 6.02, N 4.93.

***N*-(2-(4-Chlorophenyl)-1-methoxy-2-oxoethyl)-*N*-phenylformamide (10a).** Pale yellow solid, yield 12%; mp 145.1-146.3 °C; ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C): δ 8.50 (s, 1H, CHO), 6.99-7.76 (m, 9H, Ar-H), 6.92 (s, 1H, CH), 3.67 (s, 3H, OCH_3); ^{13}C NMR spectra (100 MHz, $CDCl_3$, 25 °C): δ 190.8, 163.4, 140.4, 136.8, 132.7,129.6, 129.4, 129.1, 128.3, 126.2, 82.8, 56.6; MS (ESI) *m/z* (%) = 325.7 $[M+Na]^+$. Anal. Calcd (%) for $C_{16}H_{14}ClNO_3$: C 63.27, H 4.65, N 4.61. Found: C 63.25, H 4.63, N 4.59.

X-Ray diffraction analysis for 10a (Table 3 and Figure 3)

Crystals of **10a** suitable for X-ray diffraction analysis were obtained by the slow evaporation of an EtOAc solution of **10a** at room temperature. The single crystal X-ray diffraction measurement was conducted on a Rigaku Saturn CCD area-detector diffractometer at 113(2) K using graphite monochromated Mo Kα

radiation (λ = 0.71070 Å) in the ω and φ scanning mode. An empirical absorption correction was applied using the ABSCOR program.[25] All structures were solved by direct methods using the SHELXS-97 program[26] and refined by full matrix least squares on F^2 using the SHELXL-97 program.[27] All of the hydrogen atoms were geometrically fixed using the riding model. Details, including the crystal data, data collection, and structure refinements, are summarized in Table 3. Deposition number CCDC-735378 forcompound **10a**. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Crystal data and structure refinement for **10a**

Empirical formula	$C_{16}H_{14}ClNO_3$
Formula weight	303.73
Temperature	113(2) K
Wavelength	0.71070 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 14.6024(17) Å
	b = 6.3424(6) Å
	c = 16.361(2) Å
	$\alpha = 90^o$
	$\beta = 108.336(2)^o$
	$\gamma = 90^o$
Volume	1438.3(3) $Å^3$
Z	4
Calculated density	1.403 Mg m^{-3}
Absorption coefficient	0.275 mm^{-1}
F(000)	632.0
Crystal size	0.26×0.06×0.04 mm^{-3}
θ Range for data collection	$1.63\text{-}27.86^o$
Index ranges	$-19 \le h \le 19$, $-8 \le k \le 18$, $-21 \le l \le 21$
Reflections collected/unique	17239/3420 [R_{int} = 0.0386]
Data/restraints/parameters	3420/0/192
Goodness-of-fit on F^2	1.121
R indices (all data)	R^1 = 0.0417, wR^2 = 0.1071
Extinction coefficient	0.275
Largest diff. peak and hole	0.256 and -0.462 e$Å^{-3}$

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