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A novel route to 2-imidazolin-5-one derivatives via oxidative cyclization of aryl-substituted (*Z*)-*N*-acetyl-α-dehydroalanines having a dialkylamino group

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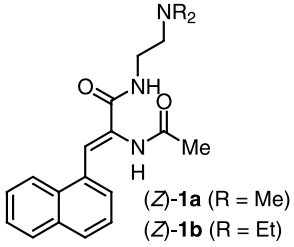
Abstract—It was found that the reaction of the title compounds [(*Z*)-**1**] with oxygen in methanol proceeds according to the first-order kinetics to give (*Z*)-2-imidazolin-5-one derivatives and hydrogen peroxide in quantitative yields. Analysis of substituent and solvent effects on the rate constant for this oxidative cyclization led us to propose that electron transfer from the dialkylamino nitrogen in (*Z*)-**1** to oxygen, amide-proton abstraction by superoxide and the subsequent intramolecular electron transfer are all rate-determining steps. The synthetic utility of the novel cyclization reaction of aryl-substituted (*Z*)-*N*-acetyl-α-dehydroalanine derivatives was discussed.

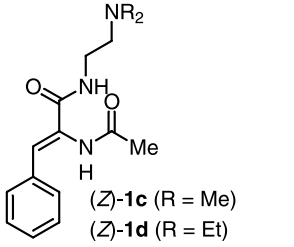
1. Introduction

In recent years much attention is being devoted to the synthetic application of photoinduced electron transfer reactions, owing to the fact that many of these reactions enable the construction of various heterocyclic rings.[1,2] In the course of our systematic study toward the characterization of the excited-state reactivities of substituted α-dehydroamino acids, we discovered an interesting photocyclization of *N*-acyl-α-dehydrophenylalanine derivatives,[3] as well as photoinduced reductive cyclization of substituted *N*-acyl-α-dehydro(1-naphthyl)alanines.[4] The former photocyclization afforded isoquinoline, 1-azetine and/or quinolinone derivatives in relatively good yields, depending on the steric bulkiness and electronic properties of the substituents introduced into the phenylalanines. The highly efficient and selective formation of dihydrobenzoquinolinone derivatives was observed through the latter electron transfer-initiated cyclization, demonstrating that *N*-acyl-α-dehydroamino acids containing a dialkylamino group or in the presence of a tertiary amine readily undergo one electron reduction to afford a radical ion pair intermediate.

Since tertiary amines are able to form charge-transfer complexes with oxygen in nonpolar solvents,[5] it is possible that the presence of oxygen in polar solvents thermally activates the tertiary amino nitrogen introduced into aryl-substituted α-dehydroalanine derivatives, thus allowing us to expect that the oxidatively activated amino nitrogen may induce a novel cyclization reaction. In a previous communication,[6] we found that the reaction of some aryl-substituted (*Z*)-*N*-acetyl-α-dehydroalanines having a dialkylamino group with oxygen in methanol gives the corresponding (*Z*)-2-imidazolin-5-one derivatives in quantitative yields. In order to expand the study of this fascinating oxidative cyclization reaction, we designed and synthesized aryl-substituted (*Z*)-*N*-acyl-α-dehydroalanines [(*Z*)-**1a**–**k**] having a 2-(dialkylamino)ethyl or a 3-(dimethylamino)propyl group attached to the carboxamide nitrogen, and investigated the substituent and solvent effects on the reactivity of (*Z*)-**1** in the presence of oxygen, hoping to shed much light on the mechanism of the novel oxidative cyclization reaction found by us.



(*Z*)-**1a** (R = Me)
(*Z*)-**1b** (R = Et)



(*Z*)-**1c** (R = Me)
(*Z*)-**1d** (R = Et)

Keywords: α-Dehydroamino acid derivatives; Oxidative cyclization; 2-Imidazolin-5-ones; Kinetics.
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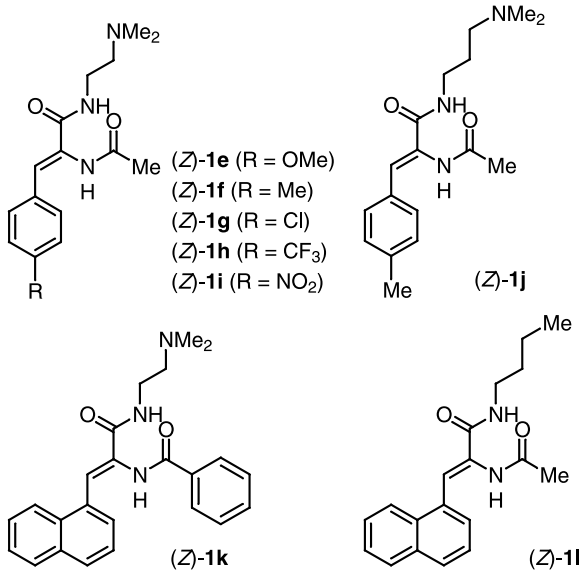


2. Results and discussion

2.1. Product analysis

The starting (*Z*)-isomers were prepared in good yields by the ring-opening reactions of aryl-substituted oxazolones with 2-(dimethylamino)ethylamine (**1a**, **1c**, **1e–i** and **1k**), 2-(diethylamino)ethylamine (**1b** and **1d**), or 3-(dimethylamino)propylamine (**1j**).[7] Each methanol solution of (*Z*)-**1** (10 mL, 1.0×10^{-4} mol dm^{-3}) was purged with air for 10 min and then heated at 80 °C in a sealed tube for a given period of time. As typically shown in Figure 1, on heating the solution in an atmosphere of air, the UV absorption of the starting **1a** at 312 nm decreased gradually with appearance of the 378 nm absorption, while there were three isosbestic points at 252, 276 and 334 nm during the reaction. Similar UV spectral changes were observed for the other derivatives, except for **1k** which exhibited a negligible change in its UV absorption under the same reaction conditions. In order to isolate the product and determine its structure, an oxygen-saturated methanol solution of (*Z*)-**1a** (100 mL, 5.0×10^{-3} mol dm^{-3}; $[O_2]=1.02\times10^{-2}$ mol dm^{-3})[8] was heated at 80 °C for 48 h in a sealed tube. The reaction mixture obtained was subjected to short column chromatography over silica gel, which allowed us to isolate 1-[2-(dimethylamino)ethyl]-2-methyl-4-(1-naphthylmethylene)-2-imidazolin-5-one (**2a**) in 95% yield. The reactions of **1b–j** with oxygen under the same conditions gave the corresponding 2-imidazolin-5-one derivatives (**2b–j**) in greater than 80% isolated yields. As shown in Figure 2, a ^{1}H NMR spectral analysis of the mixture derived from the reaction of **1c** (2.0×10^{-3} mol dm^{-3}) with oxygen in methanol confirmed that the cyclization reaction proceeds cleanly to give only **2c**. The structure of **2a–j** was determined based on their spectroscopic and physical properties including ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and HMBC spectra. In addition, the crystal structure of **2c** provided conclusive evidence for the imidazolinone ring as well as for the (*Z*)-configuration of **2** (Fig. 3),[9] indicating no occurrence of geometrical isomerization during the cyclization process of the starting (*Z*)-isomer. On the other

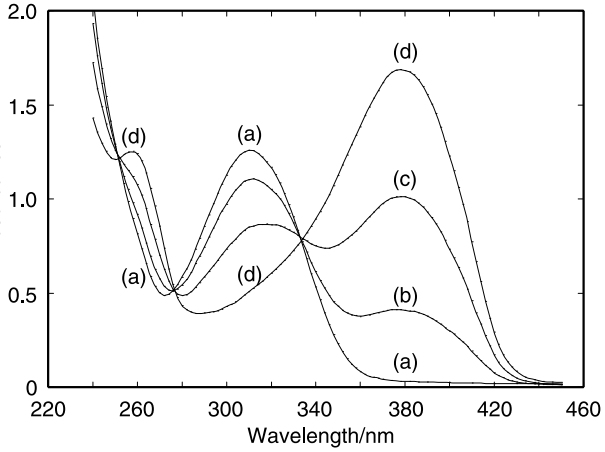


Figure 1. UV absorption spectra of air-saturated methanol solutions of (*Z*)-**1a** (1.0×10^{-4} mol dm^{-3}) heated for 0 h (curve a), 0.6 h (curve b), 1.8 h (curve c) and 24 h (curve d) at 80 °C.

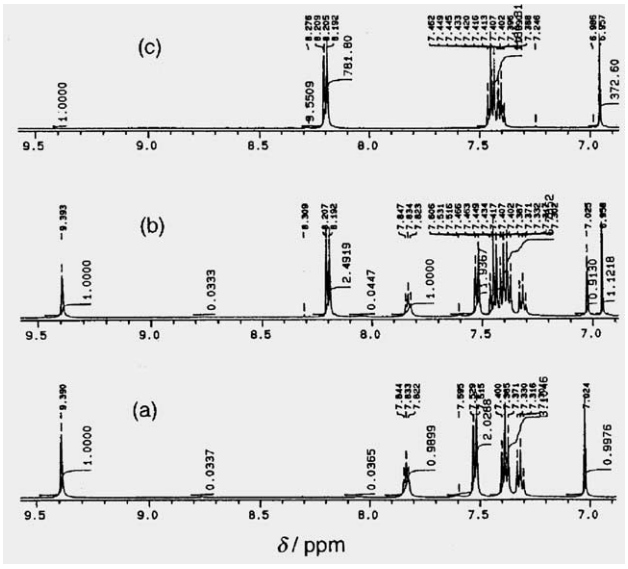


Figure 2. ^{1}H NMR spectra of dimethyl sulfoxide-d_6 solutions of the reaction mixtures obtained by heating an oxygen-saturated methanol solution of (*Z*)-**1c** (2.0×10^{-3} mol dm^{-3}) for 0 h (a), 5 h (b) and 32 h (c) at 80 °C, followed by evaporating the methanol solution to dryness.

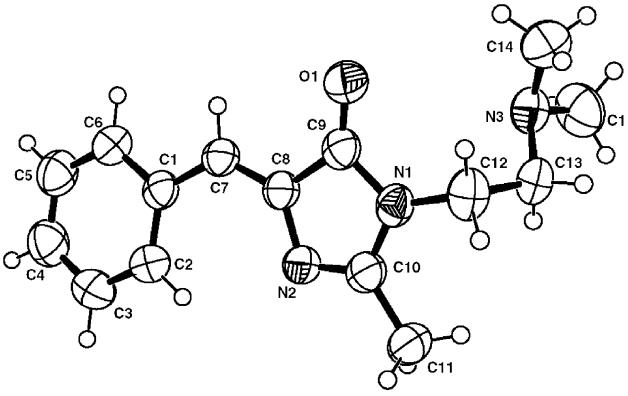
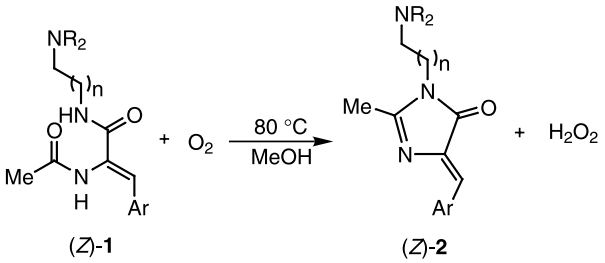


Figure 3. ORTEP drawing of (*Z*)-**2c**.



Ar = aryl; R = alkyl; n = 1,2

Scheme 1.

hand, the finding that two amide hydrogens in **1** disappear on generating **2** in the presence of oxygen strongly suggests the appearance of hydrogen peroxide as an oxygen-derived product (Scheme 1). After an oxygen-saturated methanol solution of (*Z*)-**1a** (100 mL, 5.0×10^{-3} mol dm^{-3}) was heated at 80 °C for 48 h in a sealed tube, 10 mL aliquot of the reaction mixture was diluted with an aqueous solution of KCl (10 mL, 0.20 mol dm^{-3}) and subjected to voltammetric analysis. The formation of **2a** and hydrogen peroxide in comparable yields to each other was confirmed by a comparison of oxidation currents of this sample solution (2.4 μA) and the reference solution (3.2 μA) containing **2a** and hydrogen peroxide (2.5×10^{-3} mol dm^{-3}) at 0.70 V.

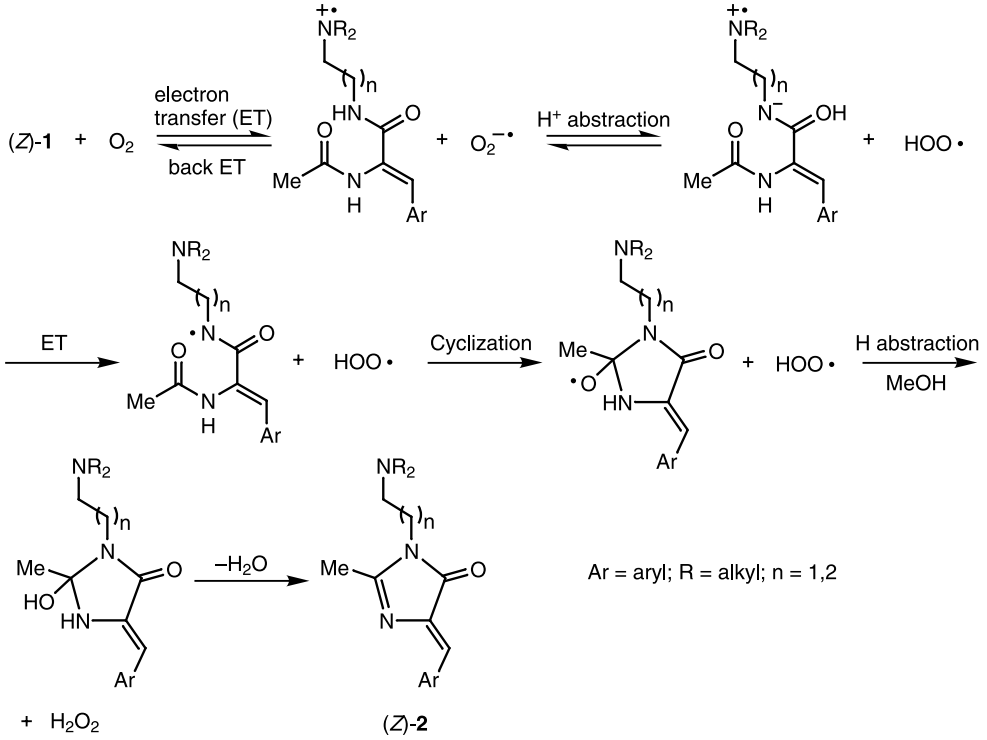
2.2. Substituent and solvent effects on the rate constant for the reaction

The findings that no reaction occurs in an atmosphere of argon and also without the dialkylamino group, like **1l**, even in oxygen-saturated methanol suggest the participation of electron transfer from the tertiary amino nitrogen to oxygen in the reaction, as already suggested. Based on the simplified Weller equation (Eq. 1),[10] where E_{ox} and E_{red} are the oxidation potential of triethylamine (0.76 V versus SCE in MeCN)[11] and the reduction potential of oxygen (−0.94 V versus SCE in MeCN),[12] respectively, free energy change in this electron transfer (ΔG_{et}) was estimated

$$\Delta G_{et}/\text{kJ mol}^{-1} = 96.5\,(E_{ox} - E_{red}) \quad (1)$$

to be 164 kJ mol^{-1}. Thus, the thermally-activated electron transfer is thermodynamically unfavorable process, allowing us to propose Scheme 2 in which reverse electron transfer affording the starting dehydroamino acids and oxygen should proceed preferentially, namely, the electron transfer equilibrium should lie greatly to the left. It is likely that the presence of the oxidized dialkylamino ($-N^{+}\cdot R_2$) and amide carbonyl groups having strong electron-withdrawing abilities in the **1**-derived cation radical enables basic superoxide to abstract the amide proton affording the amido anion and the hydroperoxyl radical.[13] Intramolecular electron transfer in the former intermediate should give the amidyl radical. The final product (*Z*)-**2** may be obtained by dehydration of the amino alcohol formed via the cyclization of this amidyl radical and the subsequent hydrogen abstraction from methanol.

Fortunately, the reaction of (*Z*)-**1** (1.0×10^{-4} mol dm^{-3}) in air-saturated methanol ($[O_2]=2.1\times10^{-3}$ mol dm^{-3})[8] at 80 °C proceeded according to the first-order kinetics in **1**, as typically shown in Figure 4. In addition, the reaction in any air-saturated solvents examined was first order in **1** (Fig. 5), so that we are able to scrutinize the substituent and solvent effects on the rate for the reaction. In Table 1 are



Scheme 2.

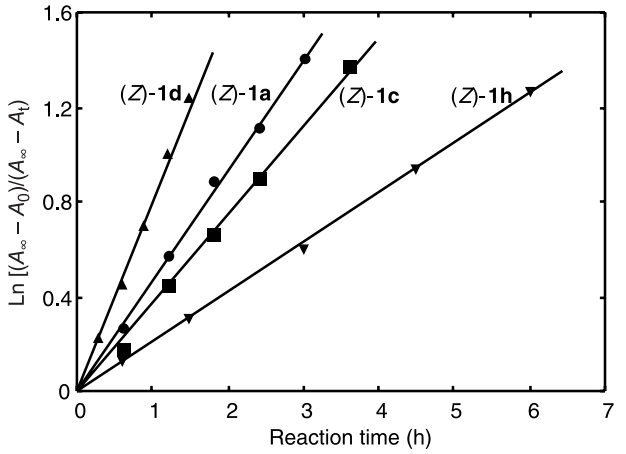


Figure 4. First-order plots for the reactions of (*Z*)-**1a** (●), (*Z*)-**1c** (■), (*Z*)-**1d** (▲) and (*Z*)-**1h** (▼, 1.0×10^{-4} mol dm^{-3}) with oxygen in air-saturated methanol at 80 °C. A_∞, A_0 and A_t refer to as the final absorbance, the initial absorbance and the absorbance after time, *t*, of the corresponding reaction mixture at a given wavelength, respectively.

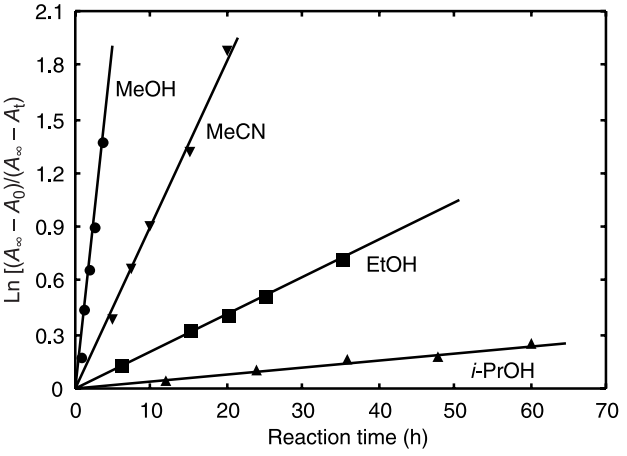


Figure 5. First-order plots for the reactions of (*Z*)-**1c** (1.0×10^{-4} mol dm^{-3}) with oxygen in air-saturated methanol(●), ethanol (■), 2-propanol (▲) and acetonitrile (▼) at 80 °C. A_∞, A_0 and A_t refer to as the final absorbance, the initial absorbance and the absorbance after time, *t*, of the reaction mixture at 348 nm, respectively.

summarized the rate constants estimated from the slopes of linear first-order plots. An inspection of the *N*-alkyl and aryl substituent effects on the reaction rate confirms that the rate constant is not much different between **1a** and **1b** and also between **1c** and **1d**. An increase in the steric bulkiness of *N*-alkyl substituent is considered to suppress attack of oxygen at the amino nitrogen and, in contrast, to enhance the stability of a cation radical intermediate ($-N^{+\cdot}R_2$). Because the former effect lowers the reaction rate which is increased by the latter effect, the result of *N*-alkyl substituent effect makes it highly probable that these two effects are compensated each other. On the other hand, the replacement of 1-naphthyl group (**1a**,**b**) by phenyl group (**1c**,**d**) exerts only a small effect on the rate constant for the reaction. Interestingly, the change in the polarity of protic solvents affects the reaction rates for both **1a** and **1c** to a much greater extent, as compared to that in the substituent R: the rate constants decrease markedly with decreasing polarity of the solvents. Furthermore, the use of acetonitrile (having almost the same polarity as methanol) as a solvent decreased the reaction rate by a factor of about 3–4.[14] The former observation is consistent with the fact that an increase in solvent polarity accelerates electron transfer reaction, and the latter observation reveals that the solvation of $-N^{+\cdot}R_2$ by the hydroxy oxygen of methanol plays a critical role in determining the reaction rate. The considerations described above, therefore, allow us to propose that electron transfer from the dialkylamino nitrogen to oxygen is a rate-determining step in the reaction sequence.

As already proposed, the combined action of the electron-withdrawing amide carbonyl and oxidized dialkylamino groups may enable basic superoxide to abstract the amide proton affording an amido anion intermediate (Scheme 2). It is, thus, predicted that addition of one more methylene spacer chain to **1f** slows down the reaction rate, owing to the increased interatomic distance between the amide and dimethylamino nitrogens. A comparison of the rate constants for **1f** and **1j** reveals that the oxidative cyclization rate of the latter is less than that of the former by a factor of 12 (Table 1). This finding is consistent with our prediction and, hence, amide-proton abstraction by superoxide, proceeding reversibly, is also a rate-determining step, as shown in Scheme 2. Interestingly, a comparison of the rate constants for **1c** and **1e–i** confirms that an increase in the electron-withdrawing ability of the substituent R has a clear tendency to decrease the reaction rate. This increase in electron-withdrawing ability is considered to accelerate amide-proton abstraction by superoxide and, in contrast, to slow down intramolecular electron transfer in an amido anion intermediate. Thus the finding that the replacement of methoxy group by electron-withdrawing trifluoromethyl or nitro group reduces the rate constant by only half strongly suggests that the effects of the substituent R on the proton abstraction and the subsequent electron transfer are compensated each other and both of these two processes are rate-determining steps. On the other hand, we previously showed that as compared to *N*-acetyl group, *N*-benzoyl group exerts a much greater steric effect on the cyclization process of substituted (*Z*)-*N*-acyl-α-dehydrophenylalanines

Table 1. Rate constants (*k*) for the reactions of (*Z*)-**1** (1.0×10^{-4} mol dm^{-3}) with oxygen at 80 °C

Compound	Solvent (ε)[a]	$[O_2]^b/10^{-3}$ mol dm^{-3}	$k/10^{-4}$ s^{-1}
1a	MeOH (32.66)	2.1	1.3
1b	MeOH		1.5
1c	MeOH		1.1
1d	MeOH		2.3
1a	EtOH (24.55)	2.1	0.12
1a	*i*-PrOH (19.92)	2.1	0.026
1a	MeCN (35.94)	1.9	0.52
1c	EtOH (24.55)		0.059
1c	*i*-PrOH (19.92)		0.012
1c	MeCN (35.94)		0.26
1e	MeOH		1.3
1f	MeOH		1.2
1g	MeOH		0.74
1h	MeOH		0.59
1i	MeOH		0.71
1j	MeOH		0.10

[a] Relative permittivity at 25 °C. See Ref. 13.
[b] See Ref. 7.

to completely inhibit the formation of isoquinoline derivatives.[3] This result allows us to speculate that the negligible formation of 2-imidazolin-5-one derivative in the reaction between **1k** and oxygen is due to a large steric hindrance of the *N*-benzoyl phenyl group to the intramolecular attack of amidyl radical on the benzoyl carbonyl moiety.

2.3. Synthetic utility of the reaction

Although many synthetic routes to 2-imidazolin-5-one derivatives are known,[15] there is no synthetic method (of these derivatives) which employs the cyclization of aryl-substituted *N*-acetyl-α-dehydroalanines activated by electron transfer to oxygen. The procedure for preparing the starting (*Z*)-α-dehydroamino acids [(*Z*)-**1**] is simple and easily applicable to its related compounds, as demonstrated in the preceding sections. In addition, the cyclodehydration reaction of (*Z*)-**1** proceeds without any dehydrating agent to quantitatively afford the corresponding (*Z*)-2-imidazolin-5-one derivatives [(*Z*)-**2**] and, hence, provides a novel and clean route to (*Z*)-**2**. Pretreatment of the concentrated reaction mixtures with a short column of silica gel is effective for obtaining (*Z*)-**2a–j** in high purities as well as in high isolated yields.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR and IR spectra were taken with a JEOL JNM-A500 spectrometer and a Hitachi 270–30 infrared spectrometer, respectively. Chemical shifts were determined using tetramethylsilane as an internal standard. UV absorption spectra were recorded on a Hitachi UV-3300 spectrophotometer. A cell with a 10-mm pathlength was used. Elemental analyses were performed on a Perkin–Elmer PE2400 series II CHNS/O analyzer. X-ray crystal data collection was performed with Mo K_α radiation (λ= 0.71069 Å) on a Rigaku RAXIS-RAPID equipped with an imaging plate. Oxidation current-potential curves were measured with a Yanaco P-1100 polarographic analyzer. Mass spectra were recorded on a JEOL 01SG-2 spectrometer. MeOH, EtOH, *i*-PrOH and MeCN were purified according to the standard procedures.[14] All other reagents used were obtained from commercial sources and of the highest grade available.

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

N-Acylglycine (0.13 mol), 1-arylaldehyde (0.15 mol) and sodium acetate (0.10 mol) were added to acetic anhydride (100 mL) and the resulting mixture was heated at 75–85 °C for 2–7 h with stirring. The mixture was cooled with ice and the solid separated out was collected by filtration with suction and washed with water, small amounts of cold EtOH and then with dry hexane. After the crude product had been air-dried at room temperature, it was recrystallized from hexane–$CHCl_3$ to give yellow crystals (30–60%). Physical and spectroscopic properties of (*Z*)-2-methyl-4-(4-methoxybenzylidene)-5(4*H*)-oxazolone, (*Z*)-2-methyl-4-(4-methybenzylidene)-5(4*H*)-oxazolone, (*Z*)-2-methyl-4-benzylidene-5(4*H*)-oxazolone, (*Z*)-2-methyl-4-(4-chlorobenzylidene)-5(4*H*)-oxazolone, (*Z*)-2-methyl-4-[4-(trifluoromethyl) benzylidene]-5(4*H*)-oxazolone, (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone and (*Z*)-2-phenyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone were consistent with those of the previously prepared samples.[3c,4d]

3.2.1. (*Z*)-2-Methyl-4-(4-nitrobenzylidene)-5(4*H*)-oxazolone. Mp 182.0–183.0 °C. IR (KBr): 1822, 1794, 1664, 1520, 1344, 1270 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.46 (3H, s), 7.14 (1H, s), 8.25 (2H, d, J=9.2 Hz), 8.28 (2H, d, J=9.2 Hz).

3.3. General procedure for the synthesis of (*Z*)-2-acetylamino-*N*-dialkylaminoalkyl-3-aryl-2-propenamides [(*Z*)-1a–j], (*Z*)-2-benzoylamino-*N*-dimethylaminoethyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1k] and (*Z*)-2-acetylamino-*N*-butyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1l]

(*Z*)-2-Methyl-4-(4-substituted benzylidene)-5(4*H*)-oxazolone (for **1c–j**), (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1a**, **1b** and **1l**), or (*Z*)-2-phenyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (for **1k**, 0.020 mol) was added to dry chloroform (200 mL) containing *N*,*N*-dialkylaminoalkylamine (for **1a–k**) or butylamine (for **1l**, 0.021 mol) and the resulting solution was allowed to stand for 1.0 h with stirring in an ice bath. The reaction mixture was concentrated to dryness and the resulting residue was dissolved in ethanol (50 mL) and then treated with activated charcoal powder. After removal of the solvent under reduced pressure, the crystalline solid obtained was recrystallized twice from ethanol–hexane affording colorless crystals (40–70%). Physical and spectroscopic properties of (*Z*)-**1l** were consistent with those of the previously prepared sample.[4c]

3.3.1. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1a]. Mp 157.5–158.5 °C. IR (KBr): 3298, 3196, 2938, 1620 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.84 (3H, s,), 2.19 (6H, s), 2.37 (2H, t, J=7.0 Hz), 3.28 (2H, dt, J=6.1, 6.7 Hz), 7.51–7.58 (5H, m), 7.90–7.96 (4H, m), 9.25 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.6, 37.3, 45.2 (2C), 58.0, 124.1, 124.2, 125.5, 126.0, 126.2,126.3, 128.35, 128.42, 131.0, 131.3, 132.5, 133.2, 164.6, 169.4. Anal. Calcd (Found) for $C_{19}H_{23}N_3O_2$: C, 70.13 (70.35); H, 7.12 (7.06); N, 12.91% (12.85%).

3.3.2. (*Z*)-2-Acetylamino-*N*-diethylaminoethyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1b]. Mp 155.0–156.0 °C. IR (KBr): 3298, 3118, 2968, 1623 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.99 (6H, t, J=7.0 Hz), 1.84 (3H, s,), 2.49–2.53 (6H, m), 3.24 (2H, dt, J=6.4, 7.0 Hz), 7.51–7.58 (5H, m), 7.90–7.95 (4H, m), 9.27 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 12.0 (2C), 22.6, 37.4, 46.7 (2C), 51.3, 124.1, 124.3, 125.5, 126.0, 126.2, 126.3, 128.35, 128.44, 131.0, 131.3, 132.5, 133.2, 164.5, 169.4. Anal. Calcd (Found) for $C_{21}H_{27}N_3O_2$: C, 71.36 (71.13); H, 7.70 (7.73); N, 11.89% (11.58%).

3.3.3. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-phenyl-2-propenamide [(*Z*)-1c]. Mp 129.0–130.0 °C. IR (KBr): 3220, 2980, 1611 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s,), 2.14 (6H, s), 2.31 (2H, t, J=6.7 Hz), 3.20 (2H, dt, J=6.1, 6.7 Hz), 7.02 (1H, s), 7.30 (1H, dd, J=7.3, 7.3 Hz), 7.37 (2H, dd, J=7.3, 7.3 Hz), 7.51 (2H, d, J=7.3 Hz), 7.83 (1H, t, J=6.1 Hz), 9.38 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 37.4, 45.2 (2C), 58.0, 127.7, 128.6 (3C), 129.3 (2C), 130.2, 134.2, 164.9, 169.5. Anal. Calcd (Found) for $C_{15}H_{21}N_3O_2$: C, 65.43 (65.50); H, 7.69 (7.42); N, 15.26% (15.47%).

3.3.4. (*Z*)-2-Acetylamino-*N*-diethylaminoethyl-3-phenyl-2-propenamide [(*Z*)-1d]. Mp 122.0–123.5 °C. IR (KBr): 3208, 2968, 1620 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 0.97 (6H, t, J=7.3 Hz), 1.99 (3H, s,), 2.47 (2H, t, J=7.6 Hz), 2.49 (4H, q, J=7.3 Hz), 3.19 (2H, dt, J=6.1, 7.6 Hz), 7.05 (1H, s), 7.32 (1H, dd, J=7.3, 7.3 Hz), 7.39 (2H, dd, J=7.3, 7.3 Hz), 7.52 (2H, d, J=7.3 Hz), 7.78 (1H, t, J=6.1 Hz), 9.40 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.9 (2C), 22.8, 37.3, 46.7 (2C), 51.3, 127.7, 128.5 (3C), 129.3 (2C), 130.1, 134.2, 164.6, 169.3. Anal. Calcd (Found) for $C_{17}H_{25}N_3O_2$: C, 67.30 (67.04); H, 8.30 (7.96); N, 13.85% (14.02%).

3.3.5. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-(4-methoxyphenyl)-2-propenamide [(*Z*)-1e]. Mp 133.5–134.5 °C. IR (KBr): 3328, 2944, 1653 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.00 (3H, s,), 2.15 (6H, s), 2.31 (2H, t, J=6.7 Hz), 3.21 (2H, dt, J=6.1, 6.7 Hz), 3.77 (3H, s), 6.95 (2H, d, J=8.6 Hz), 7.04 (1H, s), 7.50 (2H, d, J=8.6 Hz), 7.77 (1H, t, J=6.1 Hz), 9.32 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 37.3, 45.2 (2C), 55.2, 58.1, 114.0 (2C), 126.6, 127.9, 128.0, 131.0 (2C), 159.5, 165.0, 169.4. Anal. Calcd (Found) for $C_{16}H_{23}N_3O_3$: C, 62.93 (63.20); H, 7.59 (7.45); N, 13.76% (13.64%).

3.3.6. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-(4-methylphenyl)-2-propenamide [(*Z*)-1f]. Mp 130.5–131.5 °C. IR (KBr): 3214, 2986, 1671 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.99 (3H, s,), 2.16 (6H, s), 2.31 (3H, s), 2.32 (2H, t, J=6.7 Hz), 3.22 (2H, dt, J=6.1, 6.7 Hz), 7.01 (1H, s), 7.20 (2H, d, J=7.9 Hz), 7.42 (2H, d, J=7.9 Hz), 7.82 (1H, t, J=6.1 Hz), 9.35 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 20.9, 22.9, 37.3, 45.2 (2C), 58.0, 127.8, 129.1 (2C), 129.30 (2C), 129.34, 131.4, 138.1, 164.9, 169.3. Anal. Calcd (Found) for $C_{16}H_{23}N_3O_2$: C, 66.41 (66.08); H, 8.01 (7.98); N, 14.52% (14.64%).

3.3.7. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-(4-chlorophenyl)-2-propenamide [(*Z*)-1g]. Mp 132.0–133.0 °C. IR (KBr): 3214, 2980, 1656 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.98 (3H, s,), 2.15 (6H, s), 2.31 (2H, t, J=6.7 Hz), 3.22 (2H, dt, J=5.5, 6.7 Hz), 6.99 (1H, s), 7.49 (2H, d, J=8.5 Hz), 7.53 (2H, d, J=8.5 Hz), 7.91 (1H, t, J=5.5 Hz), 9.43 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 37.4, 45.2 (2C), 58.0, 125.9, 128.5 (2C), 130.8, 130.9 (2C), 132.8, 133.2, 164.6, 169.3. Anal. Calcd (Found) for $C_{15}H_{20}ClN_3O_2$: C, 58.16 (58.27); H, 6.51 (6.76); N, 13.56% (13.71%).

3.3.8. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-[4-(trifluoromethyl)phenyl]-2-propenamide [(*Z*)-1h]. Mp 131.0–132.0 °C. IR (KBr): 3400, 2980, 1659 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.99 (3H, s,), 2.16 (6H, s), 2.33 (2H, t, J=6.7 Hz), 3.23 (2H, dt, J=6.1, 6.7 Hz), 7.01 (1H, s), 7.70 (2H, d, J=7.9 Hz), 7.74 (2H, d, J=7.9 Hz), 7.99 (1H, t, J=6.1 Hz), 9.51 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.8, 37.2, 45.2 (2C), 57.9, 124.1 (1C, q, J=272 Hz), 124.9, 125.2 (2C, q, J=4 Hz), 128.0 (1C, q, J=31 Hz), 129.6 (2C), 132.3, 138.5, 164.5, 169.2. Anal. Calcd (Found) for $C_{16}H_{20}F_3N_3O_2$: C, 55.97 (55.79); H, 5.87 (6.10); N, 12.24% (12.61%).

3.3.9. (*Z*)-2-Acetylamino-*N*-dimethylaminoethyl-3-(4-nitrophenyl)-2-propenamide [(*Z*)-1i]. Mp 147.5–148.0 °C. IR (KBr): 3228, 2952, 1658, 1512, 1342 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.00 (3H, s,), 2.16 (6H, s), 2.33 (2H, t, J=6.7 Hz), 3.24 (2H, dt, J=6.4, 6.7 Hz), 7.00 (1H, s), 7.74 (2H, d, J=8.9 Hz), 8.05 (1H, t, J=6.4 Hz), 8.22 (2H, d, J=8.9 Hz), 9.60 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 22.9, 37.4, 45.2 (2C), 57.9, 123.5 (2C), 128.7, 130.1 (2C), 133.4, 141.5, 145.4, 164.5, 169.2. Anal. Calcd (Found) for $C_{15}H_{20}N_4O_4$: C, 56.24 (56.02); H, 6.29 (6.34); N, 17.49% (17.50%).

3.3.10. (*Z*)-2-Acetylamino-*N*-dimethylaminopropyl-3-(4-methylphenyl)-2-propenamide [(*Z*)-1j]. Mp 125.0–126.0 °C. IR (KBr): 3220, 2944, 1650 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 1.57 (2H, tt, J=6.7, 7.3 Hz), ?.98 (3H, s,), 2.12 (6H, s), 2.22 (2H, t, J=7.3 Hz), 2.31 (3H, s), 3.15 (2H, dt, J=6.1, 6.7 Hz), 7.01 (1H, s), 7.19 (2H, d, J=7.9 Hz), 7.42 (2H, d, J=7.9 Hz), 8.00 (1H, t, J=6.1 Hz), 9.29 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 20.8, 22.8, 26.7, 37.9, 45.1 (2C), 57.1, 127.6, 129.0 (2C), 129.2 (2C), 129.4, 131.3, 138.0, 164.7, 169.1. Anal. Calcd (Found) for $C_{17}H_{25}N_3O_2$: C, 67.30 (67.42); H, 8.30 (8.27); N, 13.85% (13.92%).

3.3.11. (*Z*)-2-Benzoylamino-*N*-dimethylaminoethyl-3-(1-naphthyl)-2-propenamide [(*Z*)-1k]. Mp 176.0–177.0 °C. IR (KBr): 3244, 3064, 2938, 1620 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 2.16 (6H, s), 2.38 (2H, t, J=6.7 Hz), 3.29 (2H, dt, J=5.5, 6.7 Hz), 7.42 (2H, dd, J=7.3, 7.9 Hz), 7.42 (1H, dd, J=7.3, 7.9 Hz), 7.51 (1H, dd, J=7.9, 7.9 Hz), 7.55 (1H, dd, J=7.3, 7.9 Hz), 7.56 (1H, dd, J=7.3, 7.9 Hz), 7.61 (1H, d, J=7.3 Hz), 7.75 (1H, s), 7.81 (2H, d, J=7.3 Hz), 7.85 (1H, d, J=7.9 Hz), 7.92 (1H, d, J=7.3 Hz), 8.02 (1H, d, J=7.9 Hz), 8.09 (1H, t, J=5.5 Hz), 9.75 (1H, s). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 37.4, 45.2 (2C), 58.0, 124.2, 125.3, 125.98, 126.03, 126.1, 126.4, 127.7 (2C), 128.1 (2C), 128.40, 128.43, 131.1, 131.4, 131.5, 132.3, 133.1, 133.8, 164.6, 166.2. Anal. Calcd (Found) for $C_{24}H_{25}N_3O_2$: C, 74.39 (74.28); H, 6.50 (6.44); N, 10.84% (10.86%).

3.4. General procedure for the reactions of (*Z*)-1 and oxygen

In order to determine the rate constant for the pseudo-first order reaction of (*Z*)-**1** with oxygen in a given solvent, each solution of (*Z*)-**1** (10 mL, 1.0×10^{-4} mol dm^{-3}) was purged with air for 10 min and sealed into a Pyrex vessel, which was immersed in an oil bath thermostated at 80 °C. At appropriate time intervals, the vessels were taken out one by one and cooled in an ice-water bath in order to stop the reaction. By following a gradual increase in the first UV absorption band of (*Z*)-**2** which appeared in the

wavelength region of 350–380 nm, the rate constant for the reaction was estimated. The UV absorption spectrum of a given solution (measured after the reaction was completed) was in nearly agreement with that of the corresponding solution of (*Z*)-**2** (1.0×10^{-4} mol dm^{-3}) isolated. Similarly, an oxygen-saturated MeOH solution of (*Z*)-**1** (10 mL, 2.0×10^{-3} mol dm^{-3}) was heated at 80 °C in a sealed tube for a given period of time and then concentrated to dryness *in vacuo*. The residue obtained was dissolved in DMSO-d_6 and subjected to the ^{1}H NMR spectral analysis.

For isolating and identifying products, a MeOH solution of (*Z*)-**1** (100 mL, 5.0×10^{-3} mol dm^{-3}) was saturated with oxygen and sealed into a Pyrex vessel, which was immersed in an oil bath thermostated at 80 °C. After completion of the reaction was confirmed by measuring the UV absorption spectrum of the mixture, 10 mL aliquot of this mixture was diluted in a volumetric flask to 20 mL with water containing 0.2 mol dm^{-3} KCl. The resulting solution was subjected to the voltammetric analysis using a glassy carbon electrode. Oxidation potentials were determined with reference to the Ag/AgCl electrode. The remaining reaction mixture was concentrated to dryness under reduced pressure and the resulting crystalline solid was subjected to short column chromatography over silica gel (230 mesh, Merck) eluting with EtOAc–MeOH (9:1 v/v) in order to obtain analytical-grade (*Z*)-**2**, which was, if necessary, recrystallized from EtOAc–hexane. Physical and spectroscopic properties of (*Z*)-2-imidazolin-5-one derivatives (**2a–j**) thus obtained are as follows.

3.4.1. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-(1-naphthylmethylene)-2-imidazolin-5-one [(*Z*)-2a]. Mp 88.0–89.0 °C. IR (KBr): 2956, 1719, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.20 (6H, s,), 2.43 (3H, s), 2.44 (2H, t, J=6.4 Hz), 3.70 (2H, t, J=6.4 Hz), 7.60 (1H, dd, J=7.3, 7.9 Hz), 7.63 (1H, dd, J=7.9, 7.9 Hz), 7.66 (1H, dd, J=7.0, 7.3 Hz), 7.72 (1H, s), 8.00 (1H, d, J=7.3 Hz), 8.02 (1H, d, J=7.3 Hz), 8.31 (1H, d, J=7.9 Hz), 8.88 (1H, d, J=7.0 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.5, 38.1, 45.3 (2C), 57.5, 119.5, 122.8, 125.6, 126.1, 127.3, 128.9, 129.5, 130.4, 130.9, 131.7, 133.3, 139.6, 165.2, 169.8. Anal. Calcd (Found) for $C_{19}H_{21}N_3O$: C, 74.24 (74.05); H, 6.89 (6.91); N, 13.67% (13.68%). HR EI-MS *m*/*z* calcd for $C_{19}H_{21}N_3O$: 307.1685. Found: 307.1685.

3.4.2. (*Z*)-1-[2-(Diethylamino)ethyl]-2-methyl-4-(1-naphthylmethylene)-2-imidazolin-5-one [(*Z*)-2b]. Mp 88.0–88.5 °C. IR (KBr): 2962, 1701, 1632 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.92 (6H, t, J=7.3 Hz), 2.44 (3H, s,), 2.50 (4H, q, J=7.3 Hz), 2.56 (2H, t, J=6.1 Hz), 3.65 (2H, t, J=6.1 Hz), 7.60 (1H, dd, J=6.7, 7.9 Hz), 7.64 (1H, dd, J=7.3, 7.3 Hz), 7.66 (1H, dd, J=7.9, 8.5 Hz), 7.72 (1H, s), 8.00 (1H, d, J=6.7 Hz), 8.01 (1H, d, J=7.3 Hz), 8.30 (1H, d, J=8.5 Hz), 8.89 (1H, d, J=7.3 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.9 (2C), 15.6, 39.1, 46.8 (2C), 50.9, 119.3, 122.8, 125.6, 126.2, 127.3, 128.9, 129.5, 130.4, 130.9, 131.7, 133.3, 139.7, 165.5, 169.9. Anal. Calcd (Found) for $C_{21}H_{25}N_3O$: C, 75.19 (75.24); H, 7.51 (7.45); N, 12.53% (12.60%).

3.4.3. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-benzylidene-2-imidazolin-5-one [(*Z*)-2c]. Mp 89.5–90.0 °C. IR (KBr): 2980, 1719, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.18 (6H, s), 2.40 (3H, s), 2.41 (2H, t, J=6.4 Hz), 3.65 (2H, t, J=6.4 Hz), 6.96 (1H, s), 7.40 (1H, dd, J=7.0, 7.0 Hz), 7.45 (2H, dd, J=7.0, 7.3 Hz), 8.20 (2H, d, J=7.3 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.5, 38.1, 45.3 (2C), 57.4, 124.7, 128.6 (2C), 129.9, 131.8 (2C), 134.1, 138.7, 164.3, 169.8. Anal. Calcd (Found) for $C_{15}H_{19}N_3O$: C, 70.01 (69.94); H, 7.44 (7.35); N, 16.33% (16.19%). HR FAB-MS *m*/*z* calcd for $C_{15}H_{20}N_3O$: 258.1606. Found: 258.1609.

3.4.4. (*Z*)-1-[2-(Diethylamino)ethyl]-2-methyl-4-benzylidene-2-imidazolin-5-one [(*Z*)-2d]. Mp 39.5–40.5 °C. IR (KBr): 2968, 1710, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.90 (6H, t, J=7.3 Hz), 2.41 (3H, s,), 2.47 (4H, q, J=7.3 Hz), 2.52 (2H, t, J=6.1 Hz), 3.60 (2H, t, J=6.1 Hz), 6.95 (1H, s), 7.40 (1H, dd, J=6.7, 6.7 Hz), 7.45 (2H, dd, J=6.7, 7.3 Hz), 8.20 (2H, d, J=7.3 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 11.9 (2C), 15.5, 39.0, 46.7 (2C), 50.8, 124.5, 128.6 (3C), 129.8, 131.8, 134.1, 138.8, 164.5, 169.9. Anal. Calcd (Found) for $C_{17}H_{23}N_3O$: C, 71.55 (71.23); H, 8.12 (7.98); N, 14.72% (14.58%).

3.4.5. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-(4-methoxybenzylidene)-2-imidazolin-5-one [(*Z*)-2e]. Mp 74.0–74.5 °C. IR (KBr): 2938, 1707, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.18 (6H, s), 2.38 (3H, s), 2.40 (2H, t, J=6.7 Hz), 3.64 (2H, t, J=6.7 Hz), 3.82 (3H, s), 6.93 (1H, s), 7.02 (2H, d, J=8.6 Hz), 8.18 (2H, d, J=8.6 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.4, 38.0, 45.3 (2C), 55.3, 57.5, 114.3 (2C), 124.9, 126.8, 133.8 (2C), 136.8, 160.7, 162.7, 169.8. Anal. Calcd (Found) for $C_{16}H_{21}N_3O_2$: C, 66.88 (67.11); H, 7.37 (7.35); N, 14.62% (14.73%).

3.4.6. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-(4-methylbenzylidene)-2-imidazolin-5-one [(*Z*)-2f]. Mp 78.5–79.0 °C. IR (KBr): 2944, 1712, 1646 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.18 (6H, s), 2.34 (3H, s), 2.39 (3H, s), 2.40 (2H, t, J=6.4 Hz), 3.65 (2H, t, J=6.4 Hz), 6.93 (1H, s), 7.26 (2H, d, J=7.9 Hz), 8.10 (2H, d, J=7.9 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.4, 21.1, 38.1, 45.3 (2C), 57.5, 124.9, 129.3 (2C), 131.4, 131.9 (2C), 138.0, 140.0, 163.6, 169.8. Anal. Calcd (Found) for $C_{16}H_{21}N_3O$: C, 70.82 (70.74); H, 7.80 (7.88); N, 15.49% (15.49%).

3.4.7. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-(4-chlorobenzylidene)-2-imidazolin-5-one [(*Z*)-2g]. Mp 115.5–116.5 °C. IR (KBr): 2980, 1713, 1644 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.18 (6H, s), 2.40 (3H, s), 2.40 (2H, t, J=6.1 Hz), 3.65 (2H, t, J=6.1 Hz), 6.97 (1H, s), 7.52 (2H, d, J=8.5 Hz), 8.23 (2H, d, J=8.5 Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.4, 38.1, 45.2 (2C), 57.4, 123.1, 128.7 (2C), 132.9, 133.3 (2C), 134.4, 139.1, 164.8, 169.6. Anal. Calcd (Found) for $C_{15}H_{18}ClN_3O$: C, 61.75 (62.01); H, 6.22 (6.35); N, 14.40% (14.70%).

3.4.8. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-[4-(trifluoromethyl)benzylidene]-2-imidazolin-5-one [(*Z*)-2h]. Mp 117.5–118.0 °C. IR (KBr): 2948, 1716, 1650 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.17 (6H, s), 2.40 (2H, t, J=6.1 Hz), 2.41 (3H, s), 3.65 (2H, t, J=

6.1 Hz), 7.02 (1H, s), 7.79 (2H, d, $J=8.5$ Hz), 8.38 (2H, d, $J=8.5$ Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.6, 38.2, 45.3 (2C), 57.4, 122.4, 124.1 (1C, q, $J=273$ Hz), 125.4 (2C, q, $J=4$ Hz), 129.1 (1C, q, $J=31$ Hz), 132.1 (2C), 138.0, 140.5, 166.2, 169.7. Anal. Calcd (Found) for $C_{16}H_{18}F_3N_3O$: C, 59.07 (58.94); H, 5.58 (5.77); N, 12.92% (12.87%).

3.4.9. (*Z*)-1-[2-(Dimethylamino)ethyl]-2-methyl-4-(4-nitrobenzylidene)-2-imidazolin-5-one [(*Z*)-2i]. Mp 137.0–138.0 °C. IR (KBr): 2980, 1716, 1641, 1508, 1340 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.18 (6H, s), 2.42 (2H, t, $J=6.1$ Hz), 2.45 (3H, s), 3.68 (2H, t, $J=6.1$ Hz), 7.08 (1H, s), 8.29 (2H, d, $J=8.5$ Hz), 8.45 (2H, d, $J=8.5$ Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.7, 38.2, 45.3 (2C), 57.3, 121.4, 123.6 (2C), 132.5 (2C), 140.6 141.3, 147.2, 167.2, 169.7. Anal. Calcd (Found) for $C_{15}H_{18}N_4O_3$: C, 59.59 (59.46); H, 6.00 (5.76); N, 18.53% (18.41%).

3.4.10. (*Z*)-1-[2-(Dimethylamino)propyl]-2-methyl-4-(4-methylbenzylidene)-2-imidazolin-5-one [(*Z*)-2j]. Oily liquid. IR (neat): 2943, 1709, 1643 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.69 (2H, tt, $J=6.9$, 7.6 Hz), 2.12 (6H, s,), 2.20 (2H, t, $J=6.9$ Hz), 2.34 (3H, s), 2.38 (3H, s), 3.58 (2H, t, $J=7.6$ Hz), 6.91 (1H, s), 7.26 (2H, d, $J=8.2$ Hz), 8.10 (2H, d, $J=8.2$ Hz). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 15.3, 21.1, 26.3, 38.2, 45.0 (2C), 56.0, 124.8, 129.3 (2C), 131.4, 131.9 (2C), 138.0, 140.0, 163.5, 169.9. Anal. Calcd (Found) for $C_{17}H_{23}N_3O$: C, 71.55 (71.38); H, 8.12 (7.87); N, 14.72% (14.54%).

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