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EFFICIENT FORMATION OF A TRIAZOLE RING *VIA* NOVEL RING-OPENING REACTION OF (*Z*)-2-METHYL-4-ARYLMETHYLENE-5(4*H*)-OXAZOLONES WITH HYDRAZIDES

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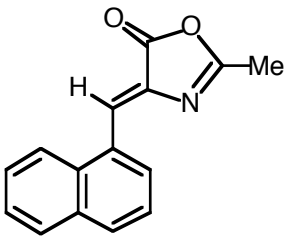
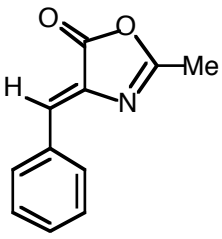
Abstract – The ring-opening mode of the title oxazolones with hydrazide nucleophiles was investigated from both synthetic and mechanistic points of view. It was found that the novel ring-opening reaction proceeded to give (*Z*)-2-(3-methyl-5-substituted 1,2,4-triazol-4-yl)-3-aryl-2-propenoic acids [1,2,4-triazole-substituted (*Z*)-α-dehydroarylalanines] as major products, along with minor or negligible amounts of their isomers. Substituent and solvent effects on the relative composition of these two isomers confirmed that this composition was dependent on steric and electronic factors of the aryl (in the oxazolones) and acyl (in the hydrazide nucleophiles) substituents as well as on solvent polarity. MM2 and PM5 calculations provided a strong piece of evidence in support of the mechanism in which the triazole ring is constructed *via* the preferential nucleophilic addition of the hydrazino nitrogen to the C=N double bond in the oxazolone ring.

INTRODUCTION

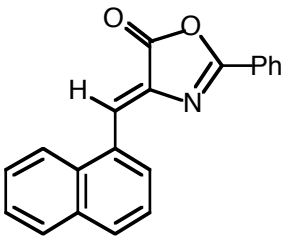
N-Acyl-α-dehydroarylalanine derivatives have been used as the starting materials in our systematic study on the photochemistry of α-dehydroamino acids,[1] being the main constituents of some antibiotics.[2] These α-dehydroalanine derivatives were prepared by the nucleophilic ring-opening reactions of substituted 5(4*H*)-oxazolones, which have made a great contribution to advances in the chemistry of α-dehydroamino acids as raw materials.[2,3] On the other hand, hydrazide derivatives have frequently been utilized as convenient building blocks for the construction of various heterocyclic ring systems but mechanism for the ring-opening reactions of the 5(4*H*)-oxazolones with hydrazides is not well understood.[4] It is, thus, of significance to explore these reactions from both synthetic and mechanistic points of view. In order to pave the way for extending our study concerning the excited-state chemistry of dehydrogenated *N*-acyl-α-dehydroarylalanine derivatives, (*Z*)-4-arylmethylene-5(4*H*)-oxazolones [(*Z*)-**1a**, (*Z*)-**1h**, and (*Z*)-**1n**] were synthesized and allowed to react with acetohydrazide and related hydrazide nucleophiles, hoping to shed much light on the mechanism of the ring-opening reactions described above (Chart 1).



(*Z*)-**1a**



(*Z*)-**1h**



(*Z*)-**1n**

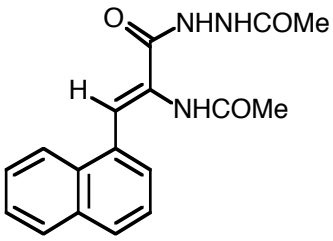


Chart 2

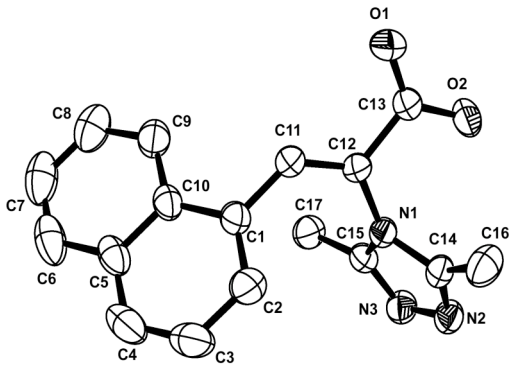
$RCONHNH_2$: R = Me, H, Ph, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$O_2NC_6H_4$, $PhCH_2$

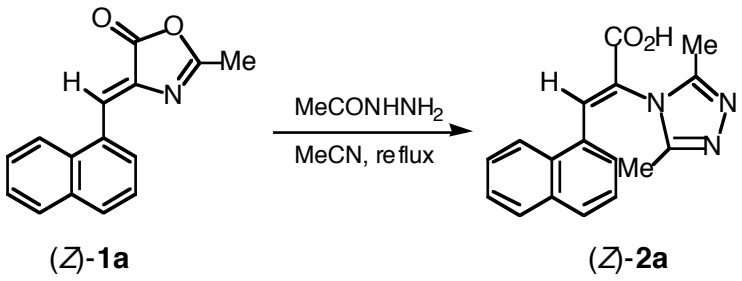
Chart 1

RESULTS AND DISCUSSION

Substituent effects

After an acetonitrile solution of (*Z*)-**1a** containing an equimolar amount of acetohydrazide was heated under reflux for 0.5 h, the reaction mixture was concentrated to dryness giving the crystalline residue whose ^{1}H NMR spectral analysis showed that the reaction proceeded cleanly without forming any by-products but not afford the ring-opening product, (*Z*)-2-acetylamino-*N'*-acetyl-3-(1-naphthyl)-2-propenehydrazide, originally expected (Chart 2). The successful growth of single crystal made it possible to establish that the novel ring-opening reaction of (*Z*)-**1a** with acetohydrazide took place to produce quantitatively (*Z*)-2-(3,5-dimethyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*Z*)-**2a**, 90% isolated yield; hereafter, referred to as 1,2,4-triazole-substituted (*Z*)-α-dehydro(1-naphthyl)alanine derivative], as shown in Figure 1 and Scheme 1.





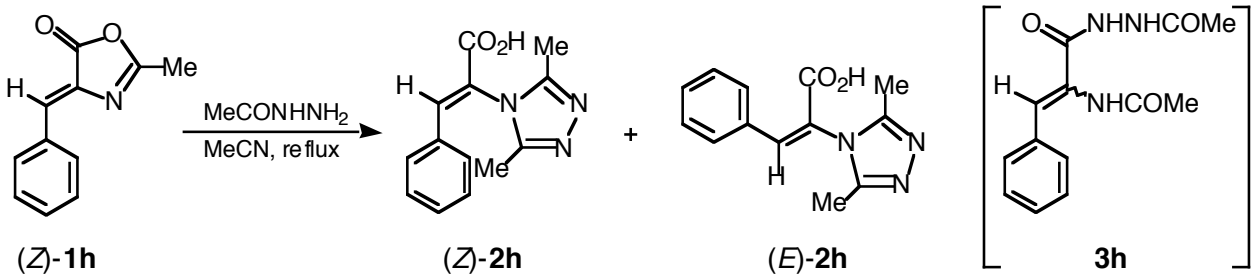
(*Z*)-**1a** (*Z*)-**2a**

Scheme 1

Figure 1. ORTEP drawing of (*Z*)-**2a**

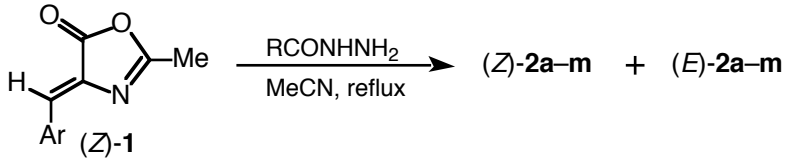
Interestingly, on treating (*Z*)-**1h** with acetohydrazide under the same reaction conditions, the corresponding (*E*)-isomer of **2** [(*E*)-**2h**] was isolated in a 7% yield, along with the (*Z*)-isomer [(*Z*)-**2h**, 88% yield] (Scheme 2 and Table 1). A careful inspection of the ^{1}H NMR spectrum of this

(*Z*)-**1h**-derived reaction mixture strongly suggested that there were minor proton signals assignable to the originally expected ring-opening products (*Z*)-**3h** and (*E*)-**3h** (Scheme 2), although attempts to isolate



Scheme 2

Table 1. Isolated yields of (*Z*)-**2** and (*E*)-**2** obtained from the reactions of (*Z*)-**1** with given hydrazide nucleophiles in refluxing acetonitrile

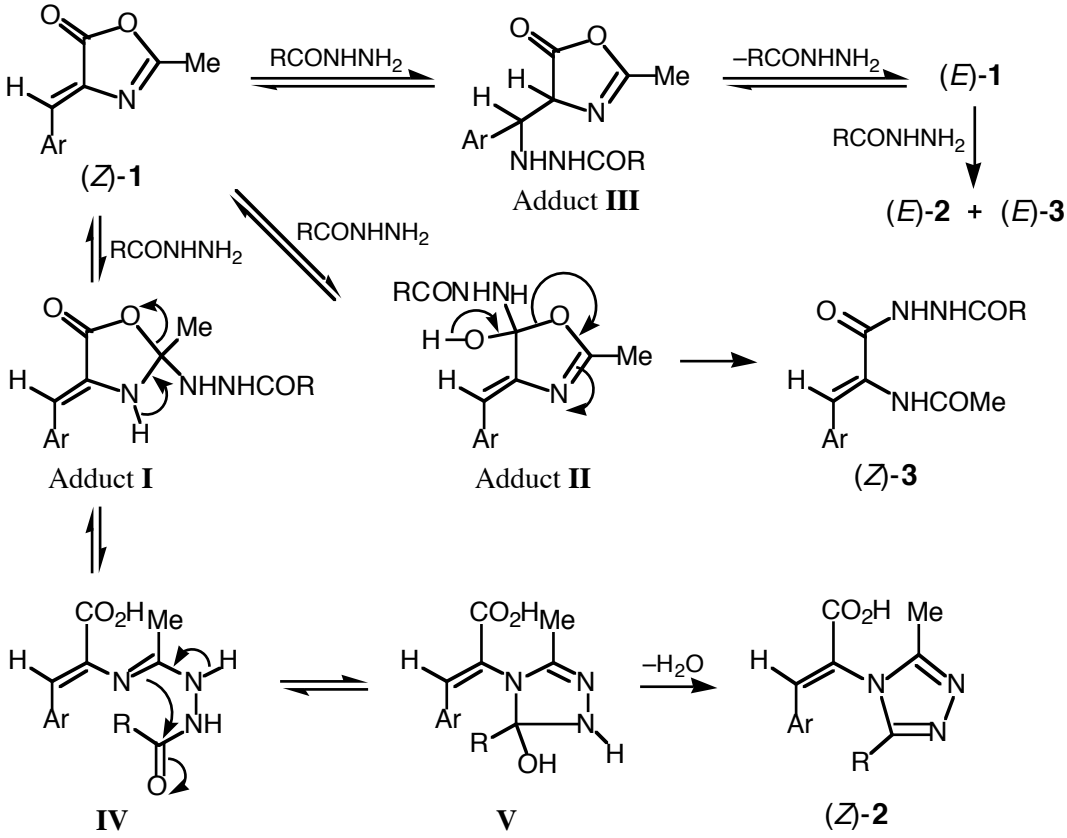


Compound	Ar	R	Reaction time (h)	Isolated yield (%)	
				(*Z*)-**2**	(*E*)-**2**
a	1-Np[a]	Me	0.5	90	—[b]
b	1-Np[a]	H	0.5	89	—[b]
c	1-Np[a]	Ph	1.0	80	—[b]
d	1-Np[a]	4-$MeOC_6H_4$	0.5	87	—[b]
e	1-Np[a]	4-NCC_6H_4	0.5	90	—[b]
f	1-Np[a]	4-$O_2NC_6H_4$	1.0	88	—[b]
g	1-Np[a]	$PhCH_2$	1.0	72	24
h	Ph	Me	0.5	88	7
i	Ph	H	0.5	97	—[b]
j	Ph	Ph	1.0	74	17
k	Ph	4-$MeOC_6H_4$	0.5	57	20
l	Ph	4-$O_2NC_6H_4$	1.0	92	—[b]
m	Ph	$PhCH_2$	1.0	75	15

[a] 1-Naphthyl. [b] Could not be detected.

these isomers were unsuccessful owing to their poor yields. As summarized in Table 1, ^{1}H NMR spectral analyses of the reactions of (*Z*)-**1a** and (*Z*)-**1h** with other hydrazide nucleophiles ($RCONHNH_2$) confirmed that while the former oxazolone gives the corresponding triazole-substituted

(*Z*)-α-dehydroarylalanines [(*Z*)-**2b–f**], except for (*Z*)-**2g**, in quantitative yields, the (*E*)-isomer is formed along with (*Z*)-**2i–m** depending on the magnitude of steric and electronic effects of the substituent R in the reactions with the latter oxazolone. It is worth noting here that (*Z*)-**2** is selectively obtained for any oxazolones on reaction with hydrazides having R= H and R= 4-$O_2NC_6H_4$.



Scheme 3

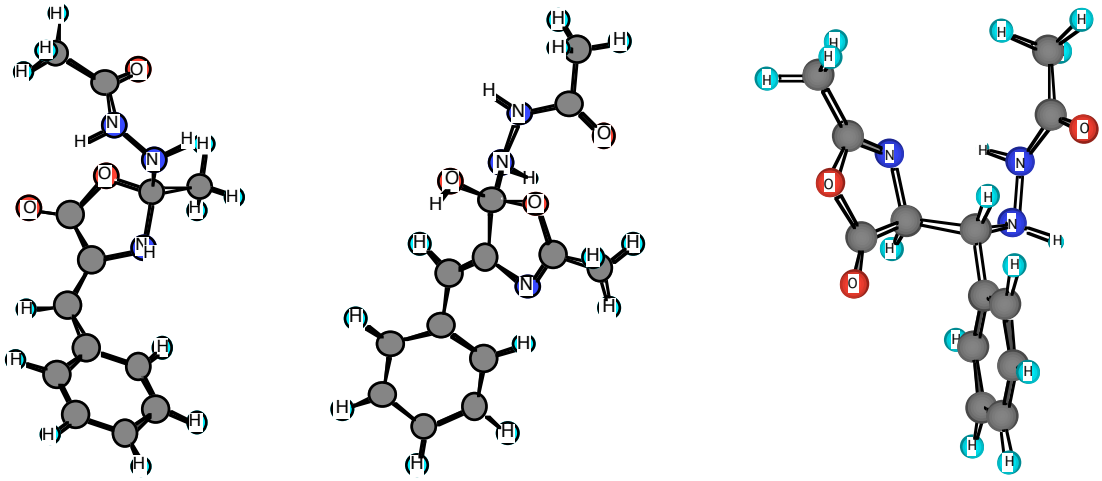
Since the presence of an equimolar amount of acetohydrazide induced negligible isomerization of (*Z*)-**2** to the corresponding (*E*)-isomer even in refluxing acetonitrile, the formation of (*Z*)-**2**, (*E*)-**2** and **3** demonstrated that 4-arylmethylene-5(4*H*)-oxazolones had three sites for the nucleophilic addition of this hydrazide. The first site should be the C=O double bond in the oxazolone ring, the second the C=N double bond in this ring and the third the arylmethylene C=C double bond, allowing us to propose Scheme 3 in order to explain the observed product distribution. In this Scheme we assumed that the adducts **I**, **II** and **III** played pivotal roles in controlling the relative composition of each product. As depicted in Scheme 3, nucleophilic addition of the hydrazino nitrogen to the C=N double bond in the ring gives the adduct **I** reversibly, the ring opening of which takes place *via* the C–O bond cleavage to form the iminomethylamino intermediate **IV**. Intramolecular nucleophilic attack of the iminomethyl nitrogen upon the acyl carbonyl carbon generates the tetrahedral intermediate **V** and then the dehydration of this intermediate eventually leads to the (*Z*)-isomer of **2**. In competition with the addition to the C=N double bond in the ring, the C=O double bond in this ring is also subject to the reversible addition of the hydrazide nucleophile to produce the adduct **II**, and the decomposition of this cyclized tetrahedral

intermediate provides the (*Z*)-isomer of **3** which is the originally expected ring-opening product. On the other hand, the finding of negligible isomerization of (*Z*)-**2** in the presence of a given hydrazide reveals that geometrical isomerization of (*Z*)-**1** into (*E*)-**1** (proceeding through the adduct **III**) must precede the nucleophilic addition to the C=N double bond of the latter isomer, which leads ultimately to (*E*)-**2** and (*E*)-**3** according to reaction pathways given for the respective isomers.

Careful inspection of the data given in Table 1 confirms that replacement of the 1-naphthyl group in (*Z*)-**1** by the phenyl has a tendency to enhance the composition of (*E*)-**2** (which can be approximated by its isolated yield) with a decrease in composition for (*Z*)-**2** and then an increase in the former composition is compensated by the lowered composition of the latter. In addition, the previous finding that the reaction of (*Z*)-**1** with primary amines selectively affords (*Z*)-*N*-acyl-α-dehydroarylalaninamides demonstrates that an intermediate (corresponding to **IV** in Scheme 3) formed in this reaction does not undergo any cyclization.[1] These substantiate reversibilities of the processes: (*Z*)-**1**→**I**→**IV**→**V**, (*Z*)-**1**→**II**, and (*Z*)-**1**→**III**→(*E*)-**1** and are also consistent with the competitive nucleophilic addition of the hydrazino nitrogen in the reaction between (*Z*)-**1** and hydrazides. It is, thus, reasonable to explain a difference in product distribution between (*Z*)-**1a** and (*Z*)-**1h** based on these reversibilities as well as on much larger steric hindrance exerted by the naphthyl group of the former in the **III**-forming step. On the other hand, molecular modeling for **IV** suggests that the substituents Ar and R are in close proximity to one another in this adduct-forming transition state. Additionally, the above suggestion leads us to predict that the composition of (*Z*)-**2** is decreased with an increase in steric bulkiness for the latter substituent: H>Me>Ph>CH_2Ph. Thus, the fact that the results are compatible with our prediction establishes that steric hindrance to the cyclization process in **IV** is one of the major factors for controlling the product composition and also that the cyclization of **IV** to **V** should be a rate-determining step. As already described above, there appeared a negligible amount of (*E*)-**2l** when (*Z*)-**1h** was allowed to react with 4-nitrobenzohydrazide (^{1}H NMR spectral analysis) whereas a certain amount of the (*E*)-isomer was isolated from the reaction with 4-methoxybenzohydrazide possessing R= 4-$MeOC_6H_4$ of almost the same steric bulkiness as R= 4-$O_2NC_6H_4$ (20% yield, Table 1). The latter substituent of much stronger electron withdrawing ability than the former is considered to assist the intramolecular nucleophilic attack of the methylimino nitrogen in **IV** upon the RCO carbonyl carbon causing the enhanced reactivity of this intermediate. It is very likely that an electronic effect on the reactivity of a given hydrazide nucleophile also contributes to the control of relative composition for (*Z*)-**2** and (*E*)-**2**, being consistent with a rate-determining step for the cyclization process: **IV**→**V**.

In order to elucidate the origin of the preferential formation of (*Z*)-**2**, energy-minimized conformations (MM2) and heats of formation (ΔH_f, PM5) of the adducts **I**, **II**, and **III** (Ar= Ph, R= Me) were calculated and shown in Figure 2. A comparison of the ΔH_f values confirms that the adduct **I** is the most stable intermediate and, hence, its formation should be the major process. This analysis reveals that the ring-opening reaction of (*Z*)-**1** with hydrazides is a thermodynamically-controlled process. In addition to substituent effects on the product composition, the above consideration is not in conflict with the reversibilities of the processes: (*Z*)-**1**→**I**, (*Z*)-**1**→**II**, and (*Z*)-**1**→**III**→(*E*)-**1** shown in Scheme 3. Surprisingly, the reaction of (*Z*)-**1n** (bearing the phenyl group at the 2-position on the oxazolone ring)

with acetohydrazide under the same reaction conditions afforded *N*-benzoyl-α-dehydronaphthylalanine derivative (**3n**) as a 6:1 mixture of the (*Z*)- and (*E*)-isomers without forming the corresponding 1,2,4-triazole-substituted α-dehydroarylalanine derivative (^{1}H NMR spectral analysis). This unexpected observation allowed us to propose that the presence of a bulky phenyl group at the 2-position exerts a great steric effect on the nucleophilic addition of the hydrazide to the C=N double bond resulting in an exclusive progress of the other two addition reactions.



I ($\Delta H_f = -290.1$ kJ mol^{-1}) **II** ($\Delta H_f = -257.0$ kJ mol^{-1}) **III** ($\Delta H_f = -272.8$ kJ mol^{-1})

Figure 2. Energy-minimized conformations and heats of formation (ΔH_f) of the adducts **I**, **II** and **III**

Solvent and temperature effects

In developing a novel reaction of synthetic utility, we have to take solvent polarity and reaction temperature into account as crucial factors affecting product compositions. For this end toluene and 1,2-dichloroethane were chosen along with acetonitrile as typical aprotic solvents. As shown in Table 2,

Table 2. Solvent and temperature effects on the isolated yields of (*Z*)-**2h** and (*E*)-**2h** obtained from the reaction of (*Z*)-**1h** and acetolhydrazide

Solvent	Reaction time (h)	Reaction temperature (°C)	Isolated yield (%)	
			(*Z*)-**2h**	(*E*)-**2h**
Toluene	2.5	80	78	13
CH_2ClCH_2Cl	8.0	22 (rt)	87	6
CH_2ClCH_2Cl	0.5	83 (reflux)	76	16
MeCN	6.5	22 (rt)	90	2
MeCN	0.5	78 (reflux)	88	7

both solvent polarity and reaction temperature affect the product composition for the (*Z*)-**1h**–acetohydrazide system to only a small extent. Somewhat different dependence of the overall

rate for each reaction pathway on these two factors is considered to be responsible for a slight change in the observed product composition. Additionally, either short column chromatography over silica gel or recrystallization from ethanol-hexane enabled the isolation of analytical-grade (*Z*)-**2** from a given reaction mixture. Therefore, we were led to conclude that the reaction of (*Z*)-2-methyl-4-arylmethylene-5(4*H*)-oxazolones with hydrazide nucleophiles in refluxing acetonitrile constitutes a novel method for the construction of a 1,2,4-triazole ring on the amino group side of (*Z*)-α-dehydroarylalanines.[4f,5]

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were taken with a JEOL JNM-ECA500 or a JEOL JNM-ECA600 spectrometer. Chemical shifts were determined using tetramethylsilane as an internal standard. IR spectra were recorded on a SHIMADZU IRPrestige-21 infrared spectrophotometer. Elemental analyses were performed on a PERKIN-ELMER PE2400 series II CHNS/O analyzer. MM2 and PM5 calculations were accomplished by using CAChe 5.0 for Windows available from Fujitsu Ltd (2002). MeCN was purified according to the standard procedure and freshly distilled prior to use.[6] 1,2-Dichloroethane and toluene were of spectroscopic grade and used as received. All other reagents were obtained from commercial sources and were of the highest grade available.

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

N-Acetylglycine or *N*-benzoylglycine (50 mmol), 1-naphthaldehyde or benzaldehyde (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 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 EtOH and then with dry hexane. After the crude product had been air-dryed at rt, it was recrystallized from hexane-$CHCl_3$ to give yellow crystals (60–70%).

(*Z*)-2-Methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone [(*Z*)-1a]. Mp 159.0–159.5 °C. IR (KBr): 1760, 1650, 1260 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (3H, s), 7.54 (1H, dd, J = 7.3, 7.9 Hz), 7.58 (1H, dd, J = 7.3, 8.6 Hz), 7.61 (1H, dd, J = 7.3, 8.6 Hz), 7.88 (1H, d, J = 7.9 Hz), 7.93 (1H, d, J = 8.6 Hz), 8.02 (1H, s), 8.24 (1H, d, J = 8.6 Hz), 8.75 (1H, d, J = 7.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 15.8, 122.8, 125.7, 126.3, 127.1, 127.4, 128.9, 129.1, 131.4, 131.8, 132.3, 133.3, 133.6, 166.8, 167.8. Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.90; H, 4.57; N, 6.19.

(*Z*)-4-Benzylidene-2-methyl-5(4*H*)-oxazolone [(*Z*)-1h]. Mp 152.0–152.5 °C. IR (KBr): 1779, 1659, 1266 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (3H, s), 7.15 (1H, s), 7.43–7.47 (3H, m), 8.06–8.09 (2H, m). ^{13}C NMR (125 MHz, DMSO-d_6): δ 15.4, 128.9 (2C), 129.8, 131.1, 131.9 (2C), 132.6, 133.0, 166.8, 167.4. Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.74; H, 4.92; N, 7.33.

(*Z*)-4-(1-Naphthylmethylene)-2-phenyl-5(4*H*)-oxazolone [(*Z*)-1n]. Mp 166.0–167.0 °C. IR (KBr): 1797, 1647, 1167 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.70–7.90 (6H, m), 8.06 (1H, d, J = 7.9 Hz), 8.08 (1H, s), 8.14 (1H, d, J = 8.6 Hz), 8.17 (2H, d, J = 7.3 Hz), 8.42 (1H, d, J = 8.6 Hz), 8.99 (1H, d, J = 7.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 123.6, 124.1, 126.2, 126.5, 127.1, 128.4, 128.7 (2C), 129.6, 129.7, 130.0 (2C), 132.0, 132.4, 132.5, 134.0, 134.5, 134.8, 164.4, 167.5. Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.01; H, 4.11; N, 4.65.

General procedure for the reactions of (*Z*)-4-Arylmethylene-2-methyl-5(4H)-oxazolone with acetohydrazide and related hydrazide nucleophiles

(*Z*)-4-Arylmethylene-2-methyl-5(4*H*)-oxazolone (2.7 mmol) and a given hydrazide nucleophile (3.2 mmol) were dissolved in MeCN (10 mL) and the resulting solution was heated under reflux for 0.5 or 1.0 h. After the solution was cooled to rt, it was concentrated to dryness under reduced pressure. The crystalline residue obtained was subjected to column chromatography over silica gel (230 mesh, Merck) eluting with EtOAc, in order to isolate analytical-grade (*Z*)-**2** and (*E*)-**2**. When the reaction mixture contained a negligible amount of the latter isomer, it was directly recrystallized from EtOH or EtOH-hexane. The reaction of (*Z*)-**1n** (2.7 mmol) with acetohydrazide (3.2 mmol) in refluxing MeCN was carried out under the same conditions as those described above and similar workup allowed us to isolate the corresponding (*Z*)-**3** as the major product. For examining solvent and temperature effects on the product composition, toluene and 1,2-dichloroethane solutions containing (*Z*)-**1h** (2.7 mmol) and acetohydrazide (3.2 mmol) were heated at 80 °C (2.5 h) and 83 °C (boiling point, 0.5 h), respectively, while these two reactants dissolved in MeCN and 1,2-dichloroethane were allowed to stand for 6.5 and 8.0 h, respectively, at rt. Physical and spectroscopic data of (*Z*)-**2a**–**m**, (*E*)-**2g**,**h**,**j**,**k**,**m**, and (*Z*)-**3n** successfully isolated are as follows.

(*Z*)-2-(3,5-Dimethyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2a]. Mp 239.5–240.0 °C. IR (KBr): 3048, 1709, 1639 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 1.99 (6H, s), 6.79 (1H, d, J = 7.6 Hz), 7.38 (1H, dd, J = 7.6, 8.3 Hz), 7.62 (1H, dd, J = 7.6, 7.6 Hz), 7.67 (1H, dd, J = 7.6, 8.3 Hz), 7.98 (1H, d, J = 7.6 Hz), 7.99 (1H, d, J = 8.3 Hz), 8.12 (1H, d, J = 8.3 Hz), 8.70 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.3 (2C), 123.4, 125.1, 125.5, 126.1, 126.8, 127.7, 128.2, 128.9, 130.8, 130.9, 133.1, 138.0, 150.5 (2C), 164.2. Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.48; H, 4.84; N, 14.18.

(*Z*)-2-(3-Methyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2b]. Mp 165.0–166.0 °C. IR (KBr): 3048, 1709, 1639 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 1.93 (3H, s), 6.94 (1H, d, J = 7.6 Hz), 7.39 (1H, dd, J = 6.9, 9.0 Hz), 7.62 (1H, dd, J = 7.6, 8.2 Hz), 7.66 (1H, dd, J = 6.9, 7.7 Hz), 7.98 (1H, d, J = 8.2 Hz), 8.00 (1H, d, J = 7.7 Hz), 8.08 (1H, d, J = 9.0 Hz), 8.48 (1H, s), 8.61 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 9.6, 123.7, 125.3, 125.8, 126.3, 126.6, 127.4, 128.5, 128.7, 130.4, 130.7, 133.0, 136.9, 144.3, 149.7, 164.1. Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.53; H, 4.99; N, 15.29.

(*Z*)-2-(3-Methyl-5-phenyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2c]. Mp 227.0–227.5 °C. IR (KBr): 3055, 1709, 1638 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.13 (3H, s), 6.76 (1H, d, *J* = 7.6 Hz), 7.25 (3H, m), 7.30 (1H, dd, *J* = 7.6, 8.3 Hz), 7.33 (2H, d, *J* = 7.6 Hz), 7.48 (1H, dd, *J* = 7.6, 7.6 Hz), 7.53 (1H, dd, *J* = 7.6, 8.3 Hz), 7.77 (1H, d, *J* = 8.3 Hz), 7.91 (1H, d, *J* = 7.6 Hz), 7.92 (1H, d, *J* = 8.3 Hz), 8.61 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.3, 123.2, 125.3, 125.7, 126.0, 126.5, 126.7 (2C), 127.1, 127.2, 128.2, 128.6 (3C), 129.6, 130.7, 130.8, 132.9, 137.5, 151.7, 153.1, 164.3. Anal. Calcd for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.16; H, 4.84; N, 11.81.

(*Z*)-2-[5-(4-Methoxyphenyl)-3-methyl-1,2,4-triazol-4-yl]-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2d]. Mp 144.0–145.0 °C. IR (KBr): 3400, 1695 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.13 (3H, s), 3.68 (3H, s), 6.73 (1H, d, *J* = 7.4 Hz), 6.77 (2H, d, *J* = 9.2 Hz), 7.21 (2H, d, *J* = 9.2 Hz), 7.34 (1H, dd, *J* = 7.4, 8.0 Hz), 7.50 (1H, dd, *J* = 6.9, 8.0 Hz), 7.55 (1H, dd, *J* = 6.9, 8.0 Hz), 7.77 (1H, d, *J* = 8.0 Hz), 7.92 (1H, d, *J* = 8.0 Hz), 7.93 (1H, d, *J* = 8.0 Hz), 8.57 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.4, 55.1, 114.0 (2C), 119.3, 123.2, 125.2, 125.5, 126.4 (2C), 127.0, 128.2 (2C), 128.4, 128.5, 130.6, 130.7, 132.9, 137.2, 151.3, 152.9, 160.1, 164.3. Anal. Calcd for $C_{23}H_{19}N_3O_3$: C, 71.68; H, 4.97; N, 10.90. Found: C, 71.40; H, 5.27; N, 11.08.

(*Z*)-2-[5-(4-Cyanophenyl)-3-methyl-1,2,4-triazol-4-yl]-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2e]. Mp 269.0–270.0 °C. IR (KBr): 3410, 2228, 1701 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.28 (3H, s), 6.69 (1H, d, *J* = 7.4 Hz), 7.27 (2H, d, *J* = 8.6 Hz), 7.33 (1H, dd, *J* = 7.4, 8.0 Hz), 7.46 (1H, dd, *J* = 7.4, 8.0 Hz), 7.54 (1H, dd, *J* = 7.4, 8.0 Hz) , 7.59 (2H, d, *J* = 8.6 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 7.93 (1H, d, *J* = 8.0 Hz), 8.59 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.5, 99.4 (2C), 112.0, 118.0, 123.2, 125.2, 125.6, 126.4, 126.9, 127.2 (2C), 128.1, 128.4, 130.3, 130.7, 130.8, 132.4, 132.7, 138.2, 151.7, 152.6, 164.1. Anal. Calcd for $C_{23}H_{16}N_4O_2$: C,72.62; H, 4.24; N, 14.73. Found: C, 72.51; H, 4.21; N, 15.05.

(*Z*)-2-[3-Methyl-5-(4-nitrophenyl)-1,2,4-triazol-4-yl]-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2f]. Mp 265.5–266.0 °C. IR (KBr): 3404, 1718, 1699, 1526, 1348 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.32 (3H, s), 6.68 (1H, d, *J* = 7.6), 7.29 (2H, d, *J* = 8.9), 7.32 (1H, dd, *J* = 7.6, 8.9 Hz), 7.33 (1H, dd, *J* = 7.6, 8.3 Hz), 7.43 (1H, dd, *J* = 7.6, 8.9 Hz), 7.57 (1H, d, *J* = 8.9 Hz), 7.84 (1H, d, *J* = 8.3 Hz), 7.91 (1H, d, *J* = 8.9 Hz), 7.91 (2H, d, *J* = 8.9 Hz), 8.57 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.5, 123.2, 123.7(2C), 125.2, 125.6, 125.8, 126.3, 126.5, 127.8(2C), 128.1, 128.4, 130.2, 130.7, 132.5, 132.7, 138.3, 147.4, 151.4, 152.8, 164.0. Anal. Calcd for $C_{22}H_{16}N_4O_4$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.80; H, 3.89; N, 14.21.

(*Z*)-2-(3-Benzyl-5-methyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*Z*)-2g]. Mp 165.0–166.0 °C. IR (KBr): 3048, 1709, 1639 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 1.99 (3H, s), 3.68 (1H, d, *J* = 15.8 Hz), 3.71 (1H, d, *J* = 15.8 Hz), 6.41 (1H, d, *J* = 7.6 Hz), 7.03 (2H, d, *J* = 6.9 Hz), 7.08 (1H, dd, *J* = 7.9, 7.9 Hz), 7.14 (2H, dd, *J* = 6.9, 7.9 Hz), 7.20 (1H, dd, *J* = 7.6, 7.6 Hz), 7.60 (1H, dd,

J = 7.6, 8.3 Hz), 7.66 (1H, dd, *J* = 7.6, 8.3 Hz), 7.90 (1H, d, *J* = 8.3 Hz), 7.97 (1H, d, *J* = 8.3 Hz), 8.10 (1H, d, *J* = 7.6 Hz), 8.57 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.3, 30.7, 123.2, 124.8, 125.3, 126.0, 126.6, 126.7, 127.6, 127.8, 128.2 (2C), 128.6 (2C), 128.9, 130.8, 130.9, 133.1, 135.4, 137.4, 151.0, 152.4, 164.0. Anal. Calcd for $C_{23}H_{19}N_3O_2$: C,74.78; H, 5.18; N, 11.37. Found: C, 74.57; H, 5.16; N, 11.53.

(*Z*)-2-(3,5-Dimethyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*Z*)-2h]. Mp 218.0–219.0 °C. IR (KBr): 3431, 1708, 1691 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.06 (6H, s), 6.95 (2H, d, *J* = 7.4 Hz), 7.39 (2H, dd, *J* = 7.4, 7.4 Hz), 7.45 (1H, dd, *J* = 7.4, 7.4 Hz), 8.09 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.1 (2C), 122.2, 129.3 (2C), 129.7 (2C), 131.3, 131.4, 139.9, 150.0 (2C), 164.4. Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 63.81; H, 5.07; N, 17.09.

(*Z*)-2-(3-Methyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*Z*)-**2i**]. Mp 245.0–246.0 °C. IR (KBr): 3424, 1711, 1698 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.09 (3H, s), 6.96 (2H, d, *J* = 6.9 Hz), 7.37 (2H, dd, *J* = 6.9, 7.6 Hz), 7.43 (1H, dd, *J* = 7.6, 7.6 Hz), 8.03 (1H, s), 8.53 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 9.4, 122.7, 129.2 (2C), 129.7 (2C), 131.1, 131.3, 139.0, 143.6, 149.6, 164.4. Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.53; H, 4.79; N, 18.41.

(*Z*)-2-(3-Methyl-5-phenyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*Z*)-2j]. Mp 205.0–206.0 °C. IR (KBr): 3058, 1714, 1642 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.15 (3H, s), 7.01 (2H, d, *J* = 7.6 Hz), 7.37 (2H, dd, *J* = 7.6, 7.6 Hz), 7.45–7.40 (4H, m), 7.53–7.51 (2H, m), 8.07 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.0, 123.3, 126.8 (2C), 127.1, 128.8 (2C), 129.3 (2C), 129.8 (2C), 129.9, 131.2, 131.5, 139.8, 151.3, 152.5, 164.4. Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76. Found: C, 70.43; H, 4.71; N, 13.76.

(*Z*)-2-[5-(4-Methoxyphenyl)-3-methyl-1,2,4-triazol-4-yl]-3-phenyl-2-propenoic acid [(*Z*)-2k]. An amorphous solid. IR (KBr): 3435, 1698, 1634 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.12 (3H, s), 3.75 (3H, s), 6.98 (2H, d, *J* = 8.9 Hz), 7.01 (2H, d, *J* = 8.9 Hz), 7.38 (2H, dd, *J* = 7.6, 8.9 Hz), 7.44 (1H, dd, *J* = 7.6, 7.6 Hz), 7.45 (2H, d, *J* = 8.9 Hz), 8.05 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.1, 55.2, 114.3 (2C), 119.4, 123.4, 128.3 (2C), 129.4 (2C), 129.9 (2C), 131.3, 131.5, 139.7, 150.8, 152.3, 160.3, 164.5. Anal. Calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found: C, 68.24; H, 5.07; N, 12.21.

(*Z*)-2-[3-Methyl-5-(4-nitrophenyl)-1,2,4-triazol-4-yl]-3-phenyl-2-propenoic acid [(*Z*)-**2l**]. Mp 266.0–267.0 °C. IR (KBr): 3446, 1762, 1703, 1531, 1339 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 2.19 (3H, s), 7.01 (2H, d, *J* = 8.2 Hz), 7.38 (2H, dd, *J* = 7.6, 8.2 Hz), 7.45 (1H, dd, *J* = 7.6, 7.6 Hz), 7.81 (2H, d, *J* = 8.9 Hz), 8.14 (1H, s), 8.29 (2H, d, *J* = 8.9 Hz). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.0, 122.7, 124.2 (2C), 127.8 (2C), 129.4 (2C), 129.8 (2C), 131.0, 131.6, 132.9, 140.4, 148.0, 151.0, 152.4, 164.1. Anal. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.03; N, 15.99. Found: C, 61.81; H, 3.76; N, 15.95.

(*Z*)-2-(5-Benzyl-3-methyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*Z*)-2m]. Mp 198.0–199.0 °C. IR (KBr): 3039, 1711, 1642 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.05 (3H, s), 3.77 (2H, s), 6.82 (2H, d, J = 7.6 Hz), 7.14–7.07 (5H, m), 7.28 (2H, dd, J = 7.6, 7.6 Hz), 7.37 (1H, dd, J = 7.6, 7.6 Hz), 7.94 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 10.1, 30.8, 126.5, 128.1 (2C), 128.8 (2C), 129.0 (2C), 129.5 (2C), 130.8, 131.5, 135.5, 138.5, 148.0, 150.3, 152.3, 164.5. Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.30; H, 5.26; N, 13.21.

(*E*)-2-(5-Benzyl-3-methyl-1,2,4-triazol-4-yl)-3-(1-naphthyl)-2-propenoic acid [(*E*)-2g]. Mp 229.0–229.5 °C. IR (KBr): 3277, 1693, 1638 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.15 (3H, s), 3.69 (2H, s), 7.29–7.27 (1H, m), 7.36–7.34(4H, m), 7.59 (1H, dd, J = 7.6, 8.3 Hz), 7.66–7.63 (2H, m), 7.82 (1H, s), 8.00 (1H, d, J = 8.3 Hz), 8.04 (1H, d, J = 7.6 Hz), 8.30 (1H, d, J = 8.9 Hz), 8.82 (1H, d, J = 7.6 Hz), 11.06 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 14.4, 30.8, 122.2, 123.3, 126.1, 126.7, 127.3, 127.8, 128.9 (2C), 129.4, 129.5 (3C), 131.3, 131.7, 132.2, 133.7, 135.2, 137.4, 164.3, 167.4, 170.4. Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.64; H, 5.05; N, 11.00.

(*E*)-2-(3,5-Dimethyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*E*)-2h]. Mp 160.0–161.0 °C. IR (KBr) : 3309, 1726, 1689 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.05 (3H, s), 2.20 (3H, s), 7.09 (1H, s), 7.44–7.48 (3H, m), 8.23 (2H, d, J= 6.9 Hz), 10.75 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 14.0, 20.2, 126.6, 128.7 (2C), 130.4, 132.1 (2C), 133.6, 136.1, 163.2, 167.0, 168.9. Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 63.88; H, 5.14; N, 17.07.

(*E*)-2-(3-Methyl-5-phenyl-1,2,4-triazol-4-yl)-3-phenyl-2-propenoic acid [(*E*)-2j]. Mp 218.0–219.0 °C. IR (KBr): 3138, 1736, 1656 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.28 (3H, s), 7.16 (1H, s), 7.51–7.45 (3H, m), 7.59 (2H, dd, J = 7.6, 7.6 Hz), 7.69 (1H, dd, J = 7.6, 7.6 Hz), 7.98 (2H, d, J = 7.6 Hz), 8.27 (2H, d, J = 6.9 Hz), 11.40 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 14.0, 126.9, 127.7 (2C), 128.7 (2C), 128.8 (2C), 130.5, 130.8, 132.2 (2C), 132.8, 133.6, 136.1, 163.1, 165.6, 167.1. Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.95; N, 13.76. Found: C, 70.82; H, 4.69; N, 13.47.

(*E*)-2-[5-(4-Methoxyphenyl)-3-methyl-1,2,4-triazol-4-yl]-3-phenyl-2-propenoic acid [(*E*)-2k]. Mp 217.5–219.0 °C. IR (KBr): 3237, 1709, 1674 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.26 (3H, s), 3.86 (3H, s), 7.12 (2H, d, J = 9.2 Hz), 7.15 (1H, s), 7.46 (1H, dd, J = 6.9, 6.9 Hz), 7.50 (2H, dd, J = 6.9, 8.0 Hz), 7.96 (2H, d, J = 9.2 Hz), 8.27 (2H, d, J = 8.0 Hz), 11.24 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 14.1, 55.5, 114.1 (2C), 122.8, 126.9, 128.8 (2C), 129.8 (2C), 130.5, 132.2 (2C), 133.7, 136.2, 162.8, 163.4, 165.1, 167.3. Anal. Calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found: C, 67.81; H, 5.28; N, 12.52.

(*E*)-2-(5-Benzyl-3-methyl-1,2,4-triazol-1-yl)-3-phenyl-2-propenoic acid [(*E*)-2m]. Mp 186.0–187.0 °C. IR (KBr): 3256, 1701, 1655 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6): δ 2.13 (3H, s), 3.69 (2H, d, J = 5.5 Hz), 7.09 (1H, s), 7.30–7.26 (1H, m), 7.36–7.35 (4H, m), 7.48–7.42 (3H, m), 8.22

(2H, d, J = 8.9 Hz), 11.02 (1H, s). ^{13}C NMR (150 MHz, DMSO-d_6): δ 13.9, 39.5, 126.7, 126.8, 128.4 (2C), 128.7 (2C), 129.0 (2C), 130.4, 132.1 (2C), 133.6, 134.7, 136.0, 163.0, 166.9, 169.9. Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.70; H, 5.11; N, 12.87.

(*Z*)-2'-Acetyl-2-benzoylamino-3-(1-naphthyl)-2-propenohydrazide [(*Z*)-3n]. Mp 222.0–223.0 °C. IR (KBr): 3252, 1647, 1608 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ 1.91 (3H, s), 7.42 (1H, dd, J = 7.6, 8.3 Hz), 7.46 (2H, dd, J = 7.6, 7.6 Hz), 7.52 (1H, dd, J = 7.6, 7.6 Hz), 7.56 (1H, dd, J = 7.6, 8.3 Hz), 7.58 (1H, dd, J = 7.6, 7.6 Hz), 7.67 (1H, d, J = 7.6 Hz), 7.76 (1H, s), 7.83 (2H, d, J = 7.6 Hz), 7.89 (1H, d, J = 8.3 Hz), 7.95 (1H, d, J = 7.6 Hz), 8.04 (1H, d, J = 8.3 Hz), 9.83 (1H, br s), 9.92 (1H, br s), 10.18 (1H, s).

X-Ray crystallographic analysis of (*Z*)-2a

A colourless prism (of the molecular formula $C_{17}H_{15}N_3O_2$) having approximate dimensions of 0.40×0.30×0.30 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ 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*;[7] Structure solution, *SIR92*;[8] Refinement, *SHELXL97*.[9]

Crystal data for (*Z*)-2a. $C_{17}H_{15}N_3O_2$, fw = 293.32; monoclinic, space group $P2_1/n$; a = 10.335(14) Å, b = 9.975(17) Å, c = 14.193(19) Å, β = 96.23(8)°, V = 1455(4) Å^3; Z = 4; D_{calcd} = 1.339 g cm^{-3}; R = 0.056, $wR(F^2)$ = 0.176. Crystallographic data (excluding these structure factors) for (*Z*)-**2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 243254. 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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