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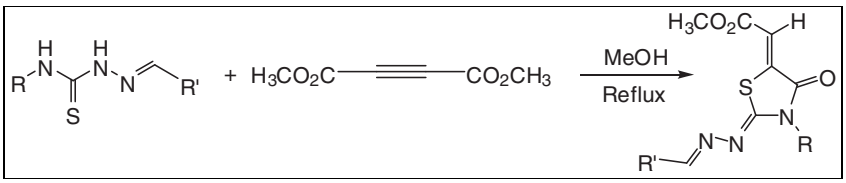

Conjugated substituted (ylidene)hydrazinecarbothioamides react in high yield with dimethyl acetylenedicarboxylate to give substituted [(ylidene)hydrazono)-4-oxothiazolidin-5-ylidene]acetates; several mechanistic options involving nucleophilic interaction are presented.

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INTRODUCTION

In recent years, there has been considerable interest in reactivity of nitrogen-containing and sulfur-containing compounds with dimethyl acetylenedicarboxylate (DMAD, **2**) [1–13]. The reaction of thioureas and thiosemicarbazide derivatives with DMAD is a convenient and effective method to prepare heterocycles possessing important biological activities. For instance, thiazolidin-4-ones represent privileged scaffolds in drug discovery [14,15]. A survey of recent articles dealing with the pharmacological properties of such compounds reveals that they display a wide range of activities [16]. Also, compounds containing 5-ylidene-1,3-thiazolidin-4-one moiety are reported to have antiviral [15], antimicrobial [17], cardiotonic [18], and anticancer activities [19–22].

Recently, we reported that the reaction of arenecarbaldehyde 4-phenylthiosemicarbazones **1a–f** with **2** gave methyl [3-aryl-4-oxo-1-(phenylthiocarbamoyl)-4,5-dihydro-1*H*-pyrazol-5-ylid-ene]ethanoates **3** (Scheme 1) [13].

RESULTS AND DISCUSSION

These intriguing transformations led us to investigate the reactions of thiosemicarbazones **4a–r** bearing a selection of aryl, alkyl, and alkenyl substituents with **2** (Fig. 1).

Compounds **4a–r** may react either with their sulfur atom, N^2 or N^4 as nucleophilic sites. On the other hand, it has been reported that the azomethine carbon and N^2 of **1** had taken part in the heterocyclization [13]. The methine carbon of **4** had to act as a nucleophile in the sense of an "umpolung" [13]. Thus, several options for interaction between **4a–r** and **2** may be expected as will be outlined later.

Treatment of **4a–r** with one molar equivalent of DMAD (**2**) in methanol at reflux resulted in the formation of single products **13a–r** in 72–89% yield. Elemental analyses and mass spectra clearly revealed that the products were formed by the addition of one molecule of DMAD to one molecule of **4a–r** with elimination of one molecule of methanol. There are possibilities for the formation of various isomers **6–9** and **11–14** that would behave spectroscopically very similar (Schemes 2–5).

If the reaction took place through N^2 and either the azomethine-CH or the SH of **4**, the most likely products would be **6** and **7**, respectively (Scheme 2).

If N^2 attacked the triple bond of **2** followed by intramolecular nucleophilic attack of N^4 at the α-ester and β-ester groups, the products **8** and **9** would be observed (Scheme 3).

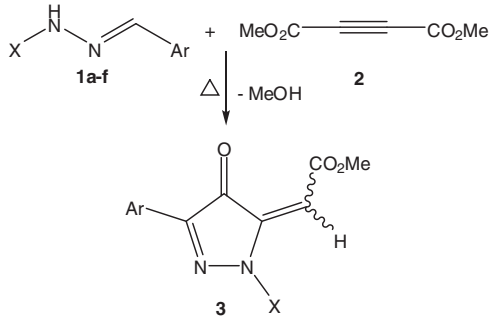
If SH attacked the triple bond of **2** followed by intramolecular nucleophilic attack of N^2 or N^4 at the β-ester carbonyl, the products **11** and **12** would be observed (Scheme 4).

The products **13** and **14** would be isolated if the reaction involve the participation of SH and N^4 or N^2, respectively (Scheme 5).

The IR spectra of the isolated compounds from the reaction of **2** with **4a–r** showed two carbonyl absorption bands about 1728–1715 and 1705–1692 cm^{-1}, and a band between 1648 and 1605 cm^{-1} that was assigned to a C=N vibration. The ^{1}H NMR spectra revealed a vinyl-CH singlet between 6.94–6.80 ppm and a methoxy singlet at about 3.91–3.78. The ^{1}H NMR signal of CH=N- is downfield shifted (δ = 8.3–7.6 ppm) because of the anisotropy of the N(sp^2) atom [23].

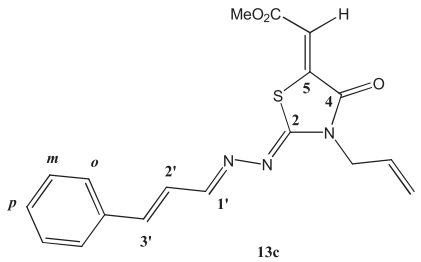
In all cases, the ^{13}C NMR spectra show five downfield lines at 166.22–163.93, 165.70–163.07, 159.92–157.75, 142.52–139.58, and 116.56–113.24 because of (C=O, ester), (C-4), (C=N), (C-5), and vinyl-CH, respectively. Full ^{1}H NMR and ^{13}C NMR data are given in the experimental part. The following additional remarks are necessary: the ^{1}H NMR spectrum of **13c** (R′=*trans*-CH=CH-Ph) shows

Scheme 1



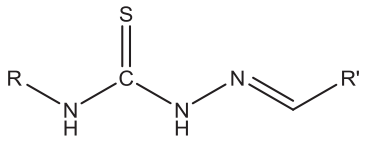
1,3: **a**, Ar = C_6H_5; **b**, Ar = 4-MeO-C_6H_4; **c**, Ar = 4-Cl-C_6H_4; **d**, Ar = 2-HO-C_6H_4; **e**, Ar = 2-Thienyl; **f**, Ar = 2-Furyl
X = Ph-NH-CS

two doublets at $\delta_H = 7.03–7.07$ ppm because of CH═CH. In its ^{13}C NMR spectrum, the ethenyl (-CH═CH-) resonates at 142.69 (C-3′) and 125.17 (C-2′). The ^1H NMR of R group in **13c** resonated at 4.54, 5.31–5.26, and 5.92 ppm because of (allyl-CH_2N), (allyl-CH_2═), and (allyl-CH═), respectively. The presence of allyl group is also evident from the ^{13}C DEPT-135 spectrum exhibiting a positive signal at 130.22 (allyl-CH═) and negative signals at 45.34 and 118.88 because of allyl-CH_2N and allyl-CH_2═, respectively.



The mass spectra showed the following four fragments common to all products [$M^+ - 31$], [$M^+ - R'CH{=}N_2$], RNCO, $m/z = 59$ (CO_2Me).

For the compound 13c. Structures **6–9** can be immediately ruled out: the four C═X ^{13}C chemical shifts are all too far upfield for a C═S. These signals must represent two C═O, one C═N, and C-5. The methoxyl protons are distinctive at $\delta_H = 3.86$; this signal gives HSQC correlation with the attached carbon at $\delta_C = 52.61$ and HMBC correlation with the ester carbonyl at $\delta_C = 166.22$ (Table 1). The signal ($\delta_C = 164.65$) giving strong HMBC correlation to vinyl-CH ($\delta_H = 6.89$) is assigned as the lactam carbonyl C-4. Under gated decoupling, this carbon couples to vinyl-CH with $J = 5.6$ Hz, a value that requires a three-bond not two-bond coupling [24]; thus, structures **11** and **12** can also be ruled out. The magnitude of this coupling further argues that C-4 and vinyl-CH are mutually *cis* [24a], as depicted in structures **13c** and **14c**. C-4 also couples to and gives HMBC correlation with the allylic methylene protons ($\delta_H = 4.54$). This is consistent with

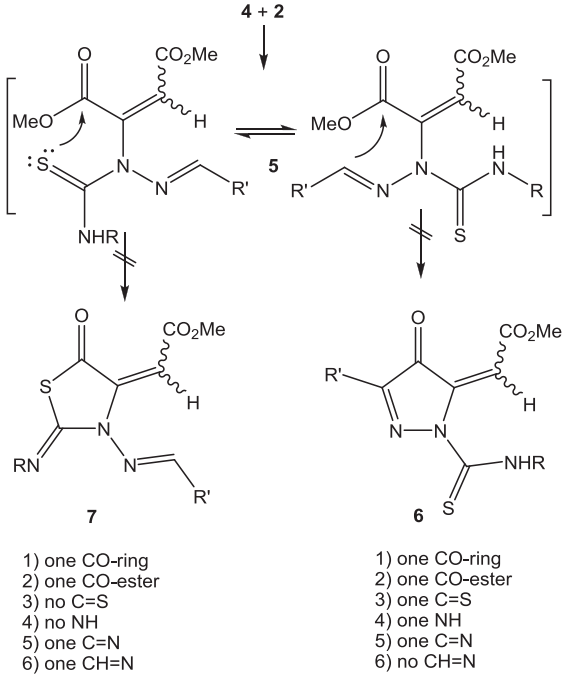


4

a, R = Ph; R' = -CH=CH-Ph (*trans*)
b, R = $PhCH_2$, R' = -CH=CH-Ph (*trans*)
c, R = CH_2=CH-CH_2, R' = -CH=CH-Ph (*trans*)
d, R = Ph, R' = -CH=CH-C_6H_4-*o*-OCH_3 (*trans*)
e, R = $PhCH_2$, R' = -CH=CH-C_6H_4-*o*-OCH_3 (*trans*)
f, R = CH_2=CH-CH_2, R' = -CH=CH-C_6H_4-*o*-OCH_3 (*trans*)
g, R = Ph, R' = -C(CH_3)=CH-Ph (*trans*)
h, R = Ph; R' = -CH=CH-$(CH_2)_2$-CH_3 (*trans*)
i, R = $PhCH_2$, R' = -CH=CH-$(CH_2)_2$-CH_3 (*trans*)
j, R = CH_2=CH-CH_2, R' = -CH=CH-$(CH_2)_2$-CH_3 (*trans*)
k, R = Ph, R' = -CH=CH-CH_3 (*trans*)
l, R = $PhCH_2$, R' = -CH=CH-CH_3 (*trans*)
m, R = CH_2=CH-CH_2, R' = -CH=CH-CH_3 (*trans*)
n, R = Ph; R' = -CH(CH_3)$_2$
o, R = $PhCH_2$, R' = -CH(CH_3)$_2$
p, R = CH_2=CH-CH_2, R' = -CH(CH_3)$_2$
q, R = Ph, R' = -CH(CH_3)C_2H_5
r, R = Ph, R' = -$(CH_2)_8$-CH_3

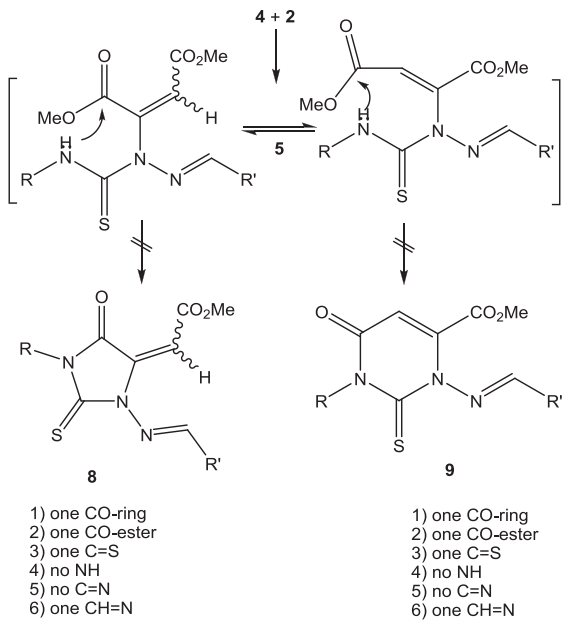
Figure 1. Substituted (ylidene)hydrazinecarbothioamides.

Scheme 2

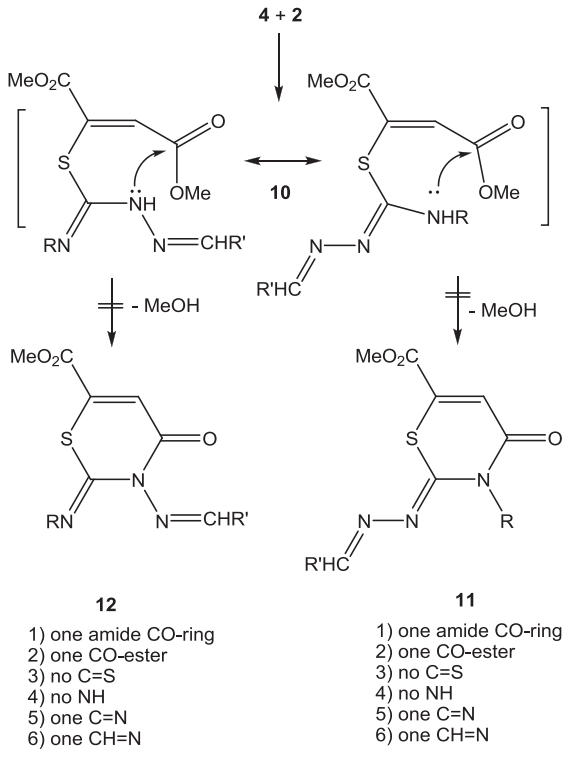


structure **13c** but excludes structure **14c**: it would be a three-bond coupling in **13c** but a five-bond coupling in **14c**. The allylic methylene carbon appears in the coupled spectrum as a well-resolved double-double-double-triplet, with three different long-range C-H coupling constants.

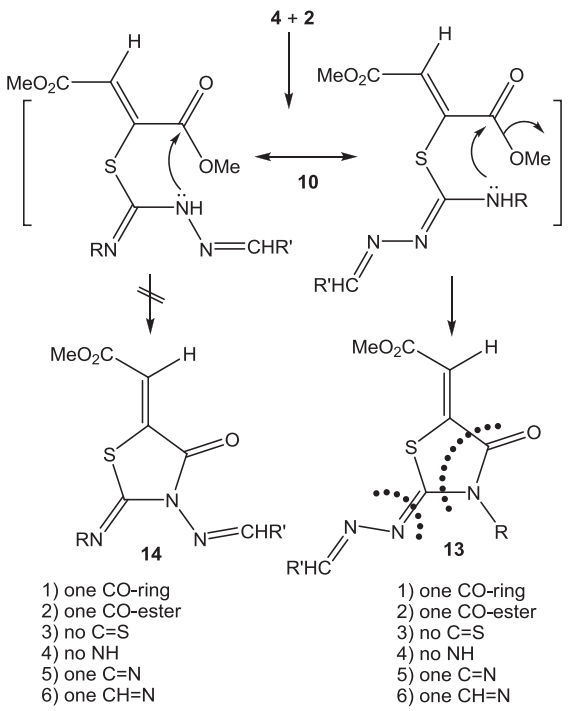
Scheme 3



Scheme 4



Scheme 5



The carbon ($\delta_C = 116.05$) giving HSQC correlation to vinyl-C*H* is assigned as vinyl-*C*H. One other carbon ($\delta_C = 141.57$) gives HMBC correlation to vinyl-C*H* (albeit weak) and is assigned as C-5 (Table 1).

The rest of the correlations and couplings are consistent with the assigned structure [25]. The long-range C-H couplings of C-*m* and C-*o* make these assignments unambiguous: C-*m* ($\delta_C = 128.90$) shows only doublet coupling to H-*m* ($\delta_H = 7.39$) on the opposite side, whereas C-*o* ($\delta_C = 127.44$) shows doublet coupling not only to the "other" H-*o* ($\delta_H = 7.52$) but also to H-*p* ($\delta_H = 7.34$) and H-3′ ($\delta_H = 7.032$). With the other cinnamylidene vinylic protons H-1′ and H-2′ ($\delta_H = 8.255$ and 7.072, respectively), H-3′ gives a classic ABX pattern [26], in which $J_{12} = 15.9$ Hz; this value establishes the stereochemistry between C-2′ and C-3′ as *trans*.

The spectral data of **13k** show methoxy protons at $\delta_H = 3.87$; this signal gives HSQC correlation with the attached carbon at $\delta_C = 52.52$ and HMBC correlation with the ester carbonyl at $\delta_C = 166.32$. The signal ($\delta_C = 164.71$) giving HMBC correlation to vinyl-CH ($\delta_H = 6.94$) is assigned as the lactam carbonyl C-4. There is no direct coupling or correlation between C-4 and the phenyl ring, so it is assigned as **13k** by analogy (Table 2).

In conclusion, all spectral data listed previously, especially the ^{13}C chemical shifts for the ring carbonyl atoms (C-1″), C=N and thiazolidine-C-5 support the formation of structures **13a–r** as the reaction products.

The NMR spectra showed that only one stereoisomer was present for all products, indicating that the reaction is stereoselective. From these data, it follows that the RNHCS group was changed; thus, the thioxo sulfur reacted as a nucleophile. One ester group was converted into a

Table 1

Spectroscopic data of compound **13c**.

^{1}H NMR ($CDCl_3$)		^{1}H-^{1}H COSY	Assignment
8.26 (AB**X**, J = 10.0, −1.8; 1H)		7.07, 7.03	H-1′
7.52 (dd, J = 7.0, 1.2; 2H)		7.39, 7.34	H-*o*
7.39 (dd, J = 7.2, 7.2; 2H)		7.52, 7.34	H-*m*
7.34 (t, J = 7.1; 1H)		7.52, 7.39	H-*p*
7.07 (**A**BX, J = 15.9, 10.0; 1H)		8.26	H-2′
7.03 (A**B**X, J = 15.9, −1.8; 1H)		8.26	H-3′
6.89 (s; 1H)			Vinyl-CH
5.92 (ddt, J_d = 16.7, 10.7, J_t = 6.0; 1H)		5.31, 5.26, 4.54	Allyl-CH═
5.31 (dd, J = 17.1, 1.0; 1H)		5.92, 5.26, *4.54*	Allyl-CH_2═ (*cis*)
5.26 (dd, J = 10.2, 0.8; 1H)		5.92, 5.31, *4.54*	Allyl-CH_2═ (*trans*)
4.54 (d, J = 5.8; 2H)		5.92, *5.31*, *5.26*	Allyl-CH_2N
3.86 (s; 3H)			OCH_3
^{13}C NMR ($CDCl_3$)	HSQC	HMBC	Assignment
166.22 (dq, J_d = 1.5, J_q = 3.5)		3.86	CO_2CH_3
164.65 (dt, J_d = 5.6, J_t = 2.9)		6.89, 4.54	C-4
161.88 (ddd, J = 162.2, 6.8, 1.4)	8.26	7.03	C-1′
158.64 (bt, J = 3.4)		8.26	C-2
142.69 (bd, J = 154.9)	7.03	8.26, 7.52, *7.39*, 7.07	C-3′
141.57 (s)		*6.89*	C-5
135.72 (dt, J_d = J_t = 6.8)		*7.52*, 7.39, 7.07	Ar-C
130.22 (ddt, J_d = 159.3, 3.3, J_t = 5.6)	5.92		Allyl-CH═
129.50 (dt, J_d = 161.3; J_t = 7.4)	7.34	7.52, 7.39	C-*p*
128.90 (dd, J = 160.9, 7.5)	7.39		C-*m*
127.44 (dddd, J = 159.1, 6.7, 6.7, 4.1)	7.52	7.39, 7.34, 7.03	C-*o*
125.17 (ddd, J = 159.3, 9.3, 3.4)	7.07	8.26, 7.032	C-2′
118.88 (ddt, J_d = 160.6, 155.2, J_t = 5.4)	5.31, 5.26	4.54	Allyl-CH_2═
116.05 (d, J = 172.3)	6.89	3.86	Vinyl-CH
52.47 (q, J = 147.6)	3.86		OCH_3
45.34 (dddt, J_d = 13.4, 8.0, 5.5, J_t = 142.3)	4.54	5.92, 5.31, 5.26	Allyl-CH_2N

lactam carbonyl, and neither the azomethine carbon nor N^1 took part in the heterocyclization.

The yield percentages of the obtained products increase in the presence of aromatic moiety. On the other hand, the thiazolidinone derivative **13q** gives a lower yield, and the reaction requires more time compared with the other derivatives.

CONCLUSION

Reactions of DMAD (**2**) with substituted (ylidene) hydrazinecarbothioamides **4a–r** having multiple bonds conjugated with the thioamide moiety should be considered separately, taking into account possible competition between nucleophilic addition of the SH group at the triple bond of the activated acetylenic compound and the methine carbon that act as a nucleophile in the sense of an "umpolung". The sulfur atom can be incorporated in the ring, and the thiaheterocycles, S-C-N + C2 or N-CS-N + C2 mode of cyclization, are favored with thiocarbohydrazides characterized by increased negative charge on sulfur atom. Comparison of ^{13}C NMR chemical shifts as well as HMBC measurements for the possible sets of isomers may serve as a useful supplementary tool in finding the correct structure of a heterocycle.

EXPERIMENTAL

General. Melting points were determined with a Gallenkamp melting point apparatus (Weiss-Gallenkamp, Loughborough, UK) and were uncorrected. The IR spectra were recorded with a Shimadzu 408 instrument (Shimadzu Corporation, Kyoto, Japan) using potassium bromide pellets. A 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were recorded on a Bruker AM 400 or AV 400 spectrometer (Bruker BioSpin, Karlsruhe, Germany, and Billerica, MA). Chemical shifts are expressed as δ (ppm) with reference of tetramethylsilane as internal standard; br, broad; s, singlet; d, doublet; t, triplet; and m, multiplet. ^{13}C assignments (q, quaternary carbon atoms) were made with the aid of DEPT 135/90 HMBC and HMQC experiments. The mass spectra (70 eV, electron impact mode) were recorded on a Finnigan MAT instrument (Thermo Finnigan, San Jose, CA). Elemental analyses were carried out at the Microanalytical Center, Cairo University, Egypt.

Starting materials.

General procedure. A solution of an aldehyde (1.0 mmol) in 5 mL dimethylsulfoxide was added dropwise with stirring at room temperature to a solution of 4-substituted thiosemicarbazide (1.0 mmol) in the same solvent containing two drops of acetic anhydride. The mixture was stirred for 3 h and left overnight. The reaction mixture was poured into 250 mL ice/water and then filtered, and the precipitates recrystallize from ethanol to give **4a–r** as colorless crystals.

N-Phenyl-2-(E)-3-phenylallylidene)hydrazinecarbothioamide (4a). This compound was obtained as colorless crystals, mp 173–175°. (Lit. 175–176°) [27]. ^{1}H NMR (DMSO-d_6): 9.95 (1H,

Table 2

Spectroscopic data of compound **13k**.

^{1}H NMR ($CDCl_3$)	^{1}H-^{1}H COSY		Assignment
7.94 (d, J = 9.4; 1H)	6.37		H-1′
7.51 (dd, J = 7.4, 7.4; 2H)	7.45, 7.38		H-*m*
7.45 (t, J = 7.3; 1H)	7.51, 7.38		H-*p*
7.38 (dd, J = 7.3, 1.4; 2H)	7.51, 7.45		H-*o*
6.94 (s; 1H)			Vinyl-CH
6.37 (ddd, J = 15.5, 9.5, 1.3; 1H)	7.94, 6.24, 1.91		H-2′
6.24 (dq, J_d = 15.4, J_q = 6.7; 1H)	6.37, 1.91		H-3′
3.87 (s; 3H)			OCH_3
1.91 (dd, J = 6.6, 0.9; 3H)	6.37, 6.24		H-4′
^{13}C NMR ($CDCl_3$)	HSQC	HMBC	Assignment
166.32 (q, J = 3.6)		3.87	CO_2CH_3
164.71 (d, J = 5.7)		6.94	C-4
162.32 (dd, J = 161.9, 8.0)	7.94	6.37, 6.24, 1.91	C-1′
159.25 (s)		7.94	C-2
142.55 (ddq, J_d = 155.4, 7.5, J_q = 4.0)	6.24	7.94, 6.37, 1.91	C-3′
141.50 (s)		6.94	C-5
133.92 (t, J = 9.4)		7.51, 7.45, 7.38	C-*ipso*
129.30 (dd, J = 163.4, 8.1)	7.51	7.51	C-*m*
129.16 (dt, J_d = 161.8, J_t = 7.6)	7.45	7.38	C-*p*
128.96 (dddq, J_d = 160.8, 9.6, 6.3, J_q = 3.2)	6.37	7.94, 6.24, 1.91	C-2′
127.64 (ddd, J = 164.0, 7.6, 5.7)	7.38	7.45, 7.38	C-*o*
116.24 (d, J = 172.6)	6.94	3.87	Vinyl-CH
52.52 (q, J = 147.7)	3.87		OCH_3
18.89 (ddq, J_d = 6.0, 4.0, J_q = 127.1)	1.91	6.37, 6.24	C-4′

br, NH), 8.02 (1H, d, J = 9.41, CH═N), 7.65–6.9 (12H, m, Ar-H and CH═CH). ^{13}C NMR (DMSO-d_6): 175.32 (C═S), 144.92 (CH═N), 139.29 and 138.92 (Ar-C), 135.85, 128.91, 128.07, 127.76, 126.94, 125.03 (Ar-CH and CH═CH). MS (EI): *m/z* (%) = 281 [M$^+$] (91), 151 (93), 135 (33), 115 (43), 91 (100), 77 (90).

N-Benzyl-2-(E)-3-phenylallylidene)hydrazinecarbothioamide (4b). This compound was obtained as colorless crystals, mp 182–184°. IR: 3365, 3133 (NH), 2995 (Ali-CH), 1625, 1579 (Ar-C═C), 1359, 971 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.82 (1H, br, NH), 8.0 (1H, d, J = 9.39, CH═N), 7.62–7.60 (2H, m, Ar-H), 7.50–7.25 (8H, m, Ar-H), 7.05–6.85 (2H, m, CH═CH), 4.85 (2H, s, CH_2-Ph). ^{13}C NMR (DMSO-d_6): 177.11 (C═S), 144.56 (CH═N), 138.86, 138.78 (Ar-C), 135.86, 129.35, 128.87, 128.17, 127.69, 127.42 (Ar-CH), 126.65, 125.05 (CH═CH), 46.55 (CH_2-Ph). MS (EI): *m/z* (%) = 295 [M$^+$] (20), 181 (36), 149 (21), 91 (100), 77 (17). *Anal*. Calcd for $C_{17}H_{17}N_3S$ (295.11): C, 69.12; H, 5.80; N, 14.22; S, 10.85. Found: C, 68.97; H, 5.91; N, 14.17; S, 11.03.

N-Allyl-2-(E)-3-phenylallylidene)hydrazinecarbothioamide (4c). This compound was obtained as colorless crystals, mp 166–167°. (Lit. 165–166°) [28]. ^{1}H NMR (DMSO-d_6): 8.46 (1H, br, NH), 7.95 (1H, d, J = 9.4, CH═N), 7.60–7.57 (2H, m, Ar-H), 7.43–7.30 (3H, m, Ar-H), 7.09–6.86 (2H, m, CH═CH), 5.93–5.90 (1H, m, allyl-CH═), 5.19–5.15 (2H, m, allyl-CH_2═), 4.22–4.20 (2H, m, allyl-CH_2N). ^{13}C NMR (DMSO-d_6): 176.86 (C═S), 144.40 (CH═N), 138.77 (Ar-C), 135.88 (allyl-CH═), 128.86, 128.79, 127.67 (Ar-CH), 126.87, 125.05 (CH═CH), 115.70 (allyl-CH_2═), 45.66 (allyl-CH_2N). MS (EI): *m/z* (%) = 245 [M$^+$] (19), 146 (22), 130 (81), 115 (100), 77 (31), 41 (86).

2-(E)-3-[(2-Methoxyphenyl)allylidene)-N-phenylhydrazinecarbothioamide (4d). This compound was obtained as colorless crystals, mp 190–192°. IR (KBr): 3315, 3236 (NH), 3123 (Ar-CH), 2983 (Ali-CH), 1619, 1594 (Ar-C═C), 1362, 983 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.95 (1H, br, NH), 8.0 (1H, d, J = 9.4, CH═N), 7.60–7.58 (3H, m, Ar-H), 7.35–7.32 (3H, m, Ar-H), 7.17–7.14 (2H, m, Ar-H), 7.10–6.90 (3H, m, CH═CH and Ar-H), 3.90 (3H, s, CH_3). ^{13}C NMR (DMSO-d_6): 175.24 (C═S), 156.42 (Ar-C-O), 145.83 (CH═N), 138.09, 134.43 (Ar-C), 130.43, 128.03, 127.80, 125.79, 124.94, 124.82, 124.13 (Ar-CH), 120.77, 110.61 (CH═CH), 55.54 (CH_3). MS (EI): *m/z* (%) = 311 [M$^+$] (100), 280 (11), 135 (36), 91 (28), 77 (21). *Anal*. Calcd for $C_{17}H_{17}N_3OS$ (311.40): C, 65.57; H, 5.50; N, 13.49; S, 10.30. Found: C, 65.65; H, 5.41; N, 13.60; S, 10.17.

N-Benzyl-2-(E)-3-[(2-methoxyphenyl)allylidene)hydrazinecarbothioamide (4e). This compound was obtained as colorless crystals, mp 210–212°. IR (KBr): 3367, 3165 (NH), 2992 (Ali-CH), 1614, 1596 (Ar-C═C), 1356, 983 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.80 (1H, br, NH), 7.98 (1H, d, J = 9.4, CH═N), 7.58–7.55 (1H, m, Ar-H), 7.30–7.20 (8H, m, Ar-H), 7.15–6.90 (2H, m, CH═CH), 4.83 (2H, s, CH_2-Ph), 3.85 (3H, s, CH_3). ^{13}C NMR (DMSO-d_6): 177.01 (C═S), 156.88 (Ar-C-O), 145.44 (CH═N), 139.26, 133.97 (Ar-C), 130.21, 128.14, 127.51, 127.40, 126.76, 125.80, 124.13 (Ar-CH), 120.73, 111.57 (CH═CH), 55.52 (CH_3), 46.52 (CH_2-Ph). MS (EI): *m/z* (%) = 325 [M$^+$] (100), 294 (22), 149 (32), 91 (40). *Anal*. Calcd for $C_{18}H_{19}N_3OS$ (325.12): C, 66.43; H, 5.88; N, 12.91; S, 9.85. Found: C, 66.28; H, 5.94; N, 13.11; S, 10.09.

N-Allyl-2-(E)-3-[(2-methoxyphenyl)allylidene)hydrazinecarbothioamide (4f). This compound was obtained as colorless crystals, mp 168–170°. IR (KBr): 3336, 3147 (NH), 3043 (Ar-CH), 2986 (Ali-CH), 1618, 1597 (Ar-C═C), 1358, 993 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.40 (1H, br, NH), 7.95 (1H, d, J = 9.4, CH═N), 7.57–7.55 (1H, m, Ar-H), 7.36–7.33 (3H, m, Ar-H), 7.10–6.90 (2H, m, CH═CH), 5.92–5.90 (1H, m, allyl-CH═), 5.15–5.12 (2H, m, allyl-CH_2═), 4.22–4.20 (2H, m, allyl-CH_2N), 3.85 (3H, s, CH_3). ^{13}C NMR (DMSO-d_6): 176.76 (C═S), 156.86 (Ar-C-

O), 145.30 (CH═N), 134.88 (allyl-CH═), 133.87 (Ar-C), 130.19, 129.06, 128.85, 125.81 (Ar-CH), 115.64 (allyl-CH_2═), 120.73, 111.55 (CH═CH), 55.70 (CH_3), 45.65 (allyl-CH_2N). MS (EI): *m/z* (%) = 275 [M^+] (18), 160 (37), 130 (100), 115 (42), 91 (28), 77 (22). *Anal*. Calcd for $C_{14}H_{17}N_3OS$ (275.37): C, 61.06; H, 6.22; N, 15.26; S, 11.64. Found: C, 60.86; H, 6.29; N, 15.11; S, 11.81.

2-(E)-2-Methyl-3-phenylallylidene)-N-phenyl hydrazinecarbothioamide (4g). This compound was obtained as colorless crystals, mp 187–189°. (Lit. 185–185.5°) [29]. ^{1}H NMR (DMSO-d_6): 9.85 (1H, br, NH), 8.0 (1H, s, CH═N), 7.59–7.18 (10H, m, Ar-H), 6.85 (1H, s, CH═), 2.20 (3H, s, CH_3). ^{13}C NMR (DMSO-d_6): 175.62 (C═S), 148.50 (CH═N), 138.98, 137.23 (Ar-C), 136.32 (═C-CH_3), 134.32, 129.35, 128.45, 128.05, 127.73, 125.53 (Ar-CH), 125.22 (CH═), 12.85 (CH_3). MS (EI): *m/z* (%) = 295 [M^+] (16), 280 (7), 135 (17), 115 (22), 91 (100), 77 (66).

2-(E)-Hex-2-enylidene-N-phenylhydrazinecarbothioamide (4h). This compound was obtained as colorless crystals, mp 152–154°. IR (KBr): 3292, 3142 (NH), 2988 (Ali-CH), 1644, 1595 (Ar-C═C), 1324, 983 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.85 (1H, br, NH), 7.85 (1H, d, *J* = 9.4, CH═N), 7.63–7.60 (2H, m, Ar-H), 7.30–7.28 (2H, m, Ar-H), 7.17–7.15 (1H, m, Ar-H), 6.22 (m, 2H, CH═CH), 2.24–2.20 (2H, m, CH_2), 1.45 (2H, m, CH_2), 0.85 (3H, t, *J* = 7.6, CH_3). ^{13}C NMR (DMSO-d_6): 175.37 (C═S), 145.21 (CH═N), 143.62 (═CH(3)), 138.96 (Ar-C), 127.98, 127.25, 124.88 (Ar-CH), 124.82 (═CH(2)), 34.38 (CH_2), 21.29 (CH_2), 13.51 (CH_3). MS (EI): *m/z* (%) = 247 [M^+] (100), 151 (76), 135 (64), 110 (51), 91 (48), 77 (41). *Anal*. Calcd for $C_{13}H_{17}N_3S$ (247.36): C, 63.12; H, 6.93; N, 16.99; S, 12.96. Found: C, 62.97; H, 7.07; N, 17.14; S, 12.79.

N-Benzyl-2-(E)-hex-2-enylidenehydrazinecarbothioamide (4i). This compound was obtained as colorless crystals, mp 165–167°. IR (KBr): 3342, 3149 (NH), 3003 (Ar-CH), 2956 (Ali-CH), 1642 (Ar-C═C), 1352, 995 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.75 (1H, br, NH), 7.80 (1H, d, *J* = 9.4, CH═N), 7.32–7.21 (5H, m, Ar-H), 6.15 (2H, m, CH═CH), 4.80 (2H, s, CH_2-Ph), 2.50 (2H, m, CH_2), 1.45 (2H, m, CH_2), 0.9 (3H, t, *J* = 7.63, CH_3). ^{13}C NMR (DMSO-d_6): 177.15 (C═S), 144.76 (CH═N), 142.94 (═CH(3)), 139.31 (Ar-C), 128.10, 127.37, 127.35 (Ar-CH), 126.62 (═CH(2)), 46.45 (CH_2-Ph), 34.31 (CH_2), 21.27 (CH_2), 13.48 (CH_3). MS (EI): *m/z* (%) = 261 [M^+] (12), 151 (16), 149 (12), 91 (51), 77 (42), 43 (100). *Anal*. Calcd for $C_{14}H_{19}N_3S$ (261.39): C, 64.33; H, 7.33; N, 16.08; S, 12.27. Found: C, 64.12; H, 7.44; N, 15.96; S, 12.15.

N-Allyl-2-(E)-hex-2-enylidenehydrazinecarbothioamide (4j). This compound was obtained as colorless crystals, mp 130–132°. IR (KBr): 3352, 3147 (NH), 2956 (Ali-CH), 1365, 998 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.30 (1H, br, NH), 7.78 (1H, d, *J* = 9.4, CH═N), 6.18–6.15 (2H, m, CH═CH), 5.94–5.90 (1H, m, allyl-CH═), 5.13–5.10 (2H, m, allyl-CH_2═), 4.15 (2H, s, allyl-CH_2N), 2.17–2.15 (2H, m, CH_2), 1.48–1.45 (2H, m, CH_2), 0.9 (3H, t, *J* = 7.65, CH_3). ^{13}C NMR (DMSO-d_6): 176.87 (C═S), 142.87 (═CH(3)), 134.94 (allyl-CH═), 127.22 (═CH(2)), 115.52 (allyl-CH_2), 45.57 (allyl-CH_2), 34.31 (CH_2), 21.28 (CH_2), 13.48 (CH_3). MS (EI): *m/z* (%) = 211 [M^+] (11), 182 (5), 115 (38), 99 (20), 41 (100). *Anal*. Calcd for $C_{10}H_{17}N_3S$ (211.33): C, 56.83; H, 8.11; N, 19.88; S, 15.17. Found: C, 57.04; H, 8.21; N, 20.06; S, 14.95.

2-(E)-But-2-enylidene-N-phenylhydrazinecarbothioamide (4k). This compound was obtained as colorless crystals, mp 144–146° (Lit. 141–143°) [30]. ^{1}H NMR (DMSO-d_6): 9.80 (1H, br, NH), 7.82 (1H, d, *J* = 9.3, CH═N), 7.58–7.55 (2H, m, Ar-H), 7.38–7.35 (2H, m, Ar-H), 7.17–7.15 (1H, m, Ar-H), 6.26–6.23 (2H, m, CH═CH), 1.85 (3H, dd, *J* = 6.6, CH_3). ^{13}C NMR (DMSO-d_6): 175.38 (C═S), 145.21 (CH═N), 141.24 (═CH(3)), 138.90 (Ar-C), 128.39, 127.99, 127.72 (Ar-CH), 125.91 (═CH (2)), 18.51 (CH_3). MS (EI): *m/z* (%) = 219 [M^+] (12), 192 (14), 151 (18), 135 (12), 77 (15), 41 (100).

2-(E)-Benzyl-2-(E)-but-2-enylidenehydrazinecarbothioamide (4l). This compound was obtained as colorless crystals, mp 150–152°. IR (KBr): 3257, 3150 (NH), 2997 (Ali-CH), 1644 (Ar-C═C), 1328, 970 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.70 (1H, br, NH), 7.75 (1H, d, *J* = 9.3, CH═N), 7.38–7.20 (5H, m, Ar-H), 6.17-6.15 (2H, m, CH═CH), 4.80 (2 H, s, CH_2-Ph), 1.83 (3H, dd, *J* = 6.6, CH_3). ^{13}C NMR (DMSO-d_6): 177.15 (C═S), 146.84 (═CH(3)), 144.78 (CH═N), 138.41 (Ar-C), 128.36, 127.52, 127.35 (Ar-CH), 126.62 (═CH(2)), 46.45 (CH_2-Ph), 18.44 (CH_3). MS (EI): *m/z* (%) = 233 [M^+] (10), 205 (5), 149 (15), 91 (100). *Anal*. Calcd for $C_{12}H_{15}N_3S$ (233.33): C, 61.77; H, 6.48; N, 18.01; S, 13.74. Found: C, 61.84; H, 6.35; N, 17.86; S, 13.89.

N-Allyl-2-(E)-but-2-enylidenehydrazinecarbothioamide (4m). This compound was obtained as colorless crystals, mp 125–126°. IR (KBr): 3354, 3149 (NH), 2938 (Ali-CH), 1375, 997 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.25 (1H, br, NH), 7.73 (1H, d, *J* = 9.3, CH═N), 6.18–6.15 (2H, m, CH═CH), 5.93–5.90 (1H, m, allyl-CH═), 5.15–5.10 (2H, m, allyl-CH_2═), 4.15 (2H, s, allyl-CH_2N), 1.85 (3H, dd, *J* = 6.63, CH_3). ^{13}C NMR (DMSO-d_6): 176.88 (C═S), 144.62 (CH═N), 141.71 (═CH(3)), 134.95 (allyl-CH═), 128.37 (═CH(2)), 115.52 (allyl-CH_2═), 45.57 (allyl-CH_2N), 18.43 (CH_3). MS (EI): *m/z* (%) 183 [M^+] (18), 115 (100), 81 (17), 41 (55). *Anal*. Calcd for $C_8H_{13}N_3S$ (183.27): C, 52.43; H, 7.15; N, 22.93; S, 17.50. Found: C, 52.62; H, 7.06; N, 23.14; S, 17.36.

2-(2-Methylpropylidene)-N-phenylhydrazinecarbothioamide (4n). This compound was obtained as colorless crystals, mp 144–146°. IR (KBr): 3301, 3151 (NH), 3064 (Ar-CH), 2998 (Ali-CH), 1599 (Ar-C═C), 1379, 981 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.70 (1H, br, NH), 7.63–7.60 (2H, m, Ar-H and CH═N), 7.52–7.50 (1H, m, Ar-H), 7.35–7.33 (2H, m, Ar-H), 7.18–7.15 (1H, m, Ar-H), 2.57–2.55 (1H, m, CH), 1.12 (6H, d, *J* = 6.5, 2CH_3). ^{13}C NMR (DMSO-d_6): 175.65 (C═S), 152.45 (CH═N), 138.94 (Ar-C), 129.47, 128.56, 125.86 (Ar-CH), 30.84 (CH), 19.89, 19.56 (CH_3). MS (EI): *m/z* (%) = 221 [M^+] (14), 178 (28), 151 (11), 135 (12), 91 (21), 77 (26), 43 (100). *Anal*. Calcd for $C_{11}H_{15}N_3S$ (221.10): C, 59.69; H, 6.83; N, 18.99; S, 14.49. Found: C, 59.82; H, 6.74; N, 19.22; S, 14.34.

N-Benzyl-2-(2-methylpropylidene)hydrazinecarbothioamide (4o). This compound was obtained as colorless crystals, mp 152–154° (Lit. 154–156°) [31]. ^{1}H NMR (DMSO-d_6): 8.60 (1H, br, NH), 7.46–7.22 (6H, m, Ar-H and CH═N), 4.85 (2H, s, CH_2-Ph), 2.57–2.54 (1H, m, CH), 1.03 (6H, d, *J* = 6.5, 2CH_3). ^{13}C NMR (DMSO-d_6): 177.39 (C═S), 151.82 (CH═N), 139.46 (Ar-C), 128.11, 127.28, 126.69 (Ar-CH), 46.42 (CH_2-Ph), 30.77 (CH), 19.60 (CH_3). MS (EI): *m/z* (%) = 235 [M^+] (18), 192 (19), 149 (10), 77 (37), 43 (100).

N-Allyl-2-(2-methylpropylidene)hydrazinecarbothioamide (4p). This compound was obtained as colorless crystals, mp 127–128°. IR (KBr): 3366, 3163 (NH), 2964 (Ali-CH), 1379, 962 (C═S, C-N str.) cm^{-1}. ^{1}H NMR (DMSO-d_6): 8.16 (1H, br, NH), 7.35 (1H, d, *J* = 9.3, CH═N), 5.94–5.90 (1H, m, allyl-CH═), 5.14–5.10 (2H, m, allyl-CH_2═), 4.23–4.20 (2H, m, allyl-CH_2N), 2.53–2.50 (1H, m, CH), 1.02 (6H, d, *J* = 6.5, 2CH_3). ^{13}C NMR (DMSO-d_6): 177.09 (C═S), 151.58 (CH═N), 135.11 (allyl-CH═), 115.43 (allyl-CH_2═), 45.53 (allyl-CH_2N), 30.74 (CH), 19.58, 19.50 (CH_3). MS (EI): *m/z* (%) = 185 [M^+] (100), 170 (11), 142 (22), 115 (38), 99 (22). *Anal*. Calcd for $C_8H_{15}N_3S$ (185.29): C, 51.86;

H, 8.16; N, 22.68; S, 17.31. Found: C, 52.07; H, 8.06; N, 22.54; S, 17.47.

2-(2-Methylbutylidene)-N-phenylhydrazinecarbothioamide (4q). This compound was obtained as colorless crystals, mp 80°. IR (KBr): 3303, 3156 (NH), 2958 (Ali-CH), 1377, 981 (C═S, C-N str.) cm^{-1}. ^1H NMR (DMSO-d_6): 9.70 (1H, br, NH), 7.60–7.55 (2H, m, Ar-H), 7.38–7.32 (1H, d, $J = 9.3$, CH═N), 7.30–7.27 (2H, m, Ar-H), 7.18–7.15 (1H, m, Ar-H), 2.35–2.32 (1H, m, CH), 1.57–1.38 (2H, m, CH_2), 1.14–1.10 (3H, d, $J = 6.6$, CH_3), 0.95–0.89 (3H, t, $J = 7.65$, CH_3). ^{13}C NMR (DMSO-d_6): 175.58 (C═S), 152.01 (CH═N), 138.93 (Ar-C), 128.50, 127.98, 125.04 (Ar-CH), 37.40 (CH), 26.83 (CH_2), 17.01 (CH_3), 11.40 (CH_3). *Anal*. Calcd for: $C_{12}H_{17}N_3S$ (235.35): C, 61.24; H, 7.28; N, 17.85; S, 13.62. Found: C, 61.33; H, 7.15; N, 18.02; S, 13.81.

2-Decylidene-N-phenylhydrazinecarbothioamide (4r). This compound was obtained as colorless crystals, mp 95°. IR (KBr): 3342, 3150 (NH), 2956–2926 (Ali-CH), 1352, 995 (C═S, C-N str.) cm^{-1}. ^1H NMR (DMSO-d_6): 9.73 (1H, br, NH), 7.63–7.55 (3H, m, Ar-H and CH═N), 7.35–7.30 (2H, m, Ar-H), 7.15–7.13 (1H, m, Ar-H), 2.3–2.26 (2H, m, CH_2), 1.45–1.40 (2H, m, CH_2-CH_3), 1.20–1.10 (12H, m, $6CH_2$), 0.94–.90 (3H, t, $J = 7.6$, CH_3). ^{13}C NMR (DMSO-d_6): 175.44 (C═S), 148.12 (CH═N), 138.96 (Ar-C), 129.36, 128.20, 125.96 (Ar-CH), 31.49, 28.91, 28.79, 28.67, 28.37, 28.07, 25.91, 22.08 (CH_2), 13.92 (CH_3). *Anal*. Calcd for: $C_{17}H_{27}N_3S$ (305.48): C, 66.84; H, 8.91; N, 13.76; S, 10.50. Found: C, 67.03; H, 9.05; N, 13.63; S, 10.62.

Products.

General procedure. A mixture of substituted (ylidene) hydrazinecarbothioamide **4a–r** (1 mmol) and DMAD (**2**, 1 mmol) in methanol was refluxed for 30 min (for compounds **4a–m**) and 2 h (for compounds **4n–r**). The solvent was evaporated, and the solid residue was recrystallized from ethanol to give **13a–r**.

(Z)-Methyl 2-((Z)-4-oxo-3-phenyl-2-{(E)-[(E)-3-phenyl-allylidene] hydrazono}thiazolidin-5-ylidene)acetate (13a). This compound was obtained as yellow crystals; mp 263–265°. IR (KBr): 1722 (CO), 1695 (COO), 1630 (C-2) and 1600 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.1 (1H, d, $J = 10.0$, CH═N), 7.5–7.28 (10H, m, Ar-CH), 6.98 (2H, d, $J = 15.9$, CH═CH), 6.90 (1H, s, cyclic-CH), 3.82 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): 166.30 (CO-ester), 164.67 (C-4), 162.24 (CH═N), 159.84 (C-2), 142.58 (═CH(3)), 141.18 (C-5), 135.63, 133.89 (Ar-C), 129.77, 129.23, 128.90, 127.74, 125.09 (Ar-CH), 125.05 (═CH(2)), 116.48 (cyclic-CH), 52.56 (OMe). MS (EI): *m/z* (%) = 391 [M^+] (82), 363 (19), 332 (4), 324 (16), 247 (12), 119 (8), 116 (42), 103 (5), 77 (10), 59 (39), 44 (100). *Anal*. Calcd for $C_{21}H_{17}N_3O_3S$ (391.44): C, 64.43; H, 4.38; N, 10.73; S, 8.19. Found: C, 64.29; H, 4.47; N, 10.89; S, 8.25.

(Z)-Methyl 2-((Z)-3-benzyl-4-oxo-2-{(E)-[(E)-3-phenyl-allylidene] hydrazono}thiazolidin-5-ylidene)acetate (13b). This compound was obtained as yellow crystals; mp 206–208°. IR (KBr): 1718 (CO), 1705 (COO), 1630 (C-2) and 1595 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.2 (1H, d, $J = 9.9$, CH═N), 7.45–7.20 (10H, m, Ar-H), 7.02 (2H, dd, $J = 15.9$, CH═CH), 6.80 (1H, s, cyclic-CH), 5.02 (2H, s, CH_2), 3.8 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): 166.22 (CO-ester), 164.98 (C-4), 161.94 (CH═N), 158.89 (C-2), 142.75 (═CH(3)), 141.57 (C-5), 135.74, 135.27 (Ar-C), 129.83, 128.99, 128.64, 128.17, 127.78, 127.46 (Ar-CH), 125.19 (═CH(2)), 116.13 (cyclic-CH), 52.49 (OMe), 46.60 (CH_2). MS (EI): *m/z* (%) = 405 [M^+] (100), 374 (10), 346 (5), 302 (10), 272 (18), 261 (34), 219 (25), 144 (14), 133 (26), 91 (58), 59 (36), 44 (61). *Anal*. Calcd for $C_{22}H_{19}N_3O_3S$ (405.47): C, 65.17; H, 4.72; N, 10.36; S, 7.91. Found: C, 64.97; H, 4.81; N, 10.52; S, 8.04.

(Z)-Methyl 2-((Z)-3-allyl-4-oxo-2-{(E)-[(E)-3-phenylallylidene]-hydrazono}thiazolidin-5-ylidene)acetate (13c). This compound was obtained as yellow crystals; mp 150°. IR (KBr): 1715 (CO), 1700 (COO), 1630 (C-2) and 1605 (Ar-C═C) cm^{-1}. ^1H NMR and ^{13}C NMR (see Table 1). MS (EI): *m/z* (%) = 355 [M^+] (100), 324 (6), 280 (12), 211 (16), 168 (10), 144 (8), 130 (36), 116 (46), 83 (11), 77 (13), 59 (7), 41 (12). *Anal*. Calcd for $C_{18}H_{17}N_3O_3S$ (355.41): C, 60.83; H, 4.82; N, 11.82; S, 9.02. Found: C, 61.03; H, 4.74; N, 12.01; S, 8.87.

(Z)-Methyl 2-((Z)-2-{(E)-[(E)-3-(2-methoxy-phenyl)allylidene]-hydrazono}-4-oxo-3-phenylthiazolidin-5-ylidene)acetate (13d). This compound was obtained as yellow crystals; mp 278–280°. IR (KBr): 1722 (CO), 1700 (COO), 1615 (C-2) and 1600 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.18 (1H, d, $J = 9.9$, CH═N), 7.61–7.39 (9H, m, Ar-H), 6.97 (2H, d, $J = 15.9$, CH═CH), 6.89 (1H, s, cyclic-CH), 3.90 (3H, s, CH_3), 3.87 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): 166.03 (CO-ester), 164.77 (C-4), 161.34 (CH═N), 157.85 (Ar-C-O), 157.55 (C-2), 141.23 (C-5), 138.42 (═CH(3)), 134.99 (Ar-C), 130.73 (Ar-C), 129.80, 129.17, 127.88, 127.64, 125.56 (Ar-CH), 120.83 (═CH(2)), 115.62 (cyclic-CH), 55.51, 51.63 (CH_3). MS (EI): *m/z* (%) = 421 [M^+] (19), 390 (48), 356 (7), 261 (5), 247 (8), 146 (6), 119 (8), 103 (6), 91 (10), 77 (9), 59 (54), 44 (100). *Anal*. Calcd for $C_{22}H_{19}N_3O_4S$ (421.47): C, 62.69; H, 4.54; N, 9.97; S, 7.61. Found: C, 62.54; H, 4.43; N, 10.11; S, 7.77.

(Z)-Methyl 2-((Z)-3-benzyl-2-{(E)-[(E)-3-(2-methoxyphenyl)-allylidene]hydrazono}-4-oxothiazolidin-5-ylidene)acetate (13e). This compound was obtained as yellow crystals; mp 192–194°. IR (KBr): 1720 (CO), 1700 (COO), 1620 (C-2) and 1600 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.3 (1H, d, $J = 9.9$, CH═N), 7.55–7.30 (9H, m, Ar-H), 7.0–6.92 (2H, d, $J = 15.9$, CH═CH), 6.9 (1H, s, cyclic-CH), 5.10 (2H, s, CH_2), 3.9 (3H, s, CH_3), 3.88 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): 165.73 (CO-ester), 164.47 (C-4), 162.44 (CH═N), 157.75 (Ar-C-O), 157.06 (C-2), 141.21 (C-5), 137.5 (═CH (3)), 134.77 (Ar-C), 130.19 (Ar-C), 128.40, 128.09, 127.61, 127.29, 127.56, 125.11 (Ar-CH), 120.34 (═CH(2)), 115.42 (cyclic-CH), 55.01, 51.93 (CH_3), 46.05 (CH_2). MS (EI): *m/z* (%) = 435 [M^+] (41), 404 (92), 376 (4), 345 (8), 275 (9), 261 (12), 174 (5), 133 (14), 91 (44), 59 (39), 44 (100). *Anal*. Calcd for $C_{23}H_{21}N_3O_4S$ (435.13): C, 63.43; H, 4.86; N, 9.65; S, 7.63. Found: C, 63.61; H, 4.94; N, 9.48; S, 7.49.

(Z)-Methyl 2-((Z)-3-allyl-2-{(E)-[(E)-3-(2-methoxyphenyl)-allylidene]hydrazono}-4-oxothiazo-lidin-5-ylidene)acetate (13f). This compound was obtained as yellow crystals; mp 208–210°. IR (KBr): 1715 (CO), 1700 (COO), 1630 (C-2) and 1605 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.25 (1H, d, $J = 9.9$, CH═N), 7.68–7.30 (4H, m, Ar-H), 7.0–6.92 (2H, d, $J = 15.9$, CH═CH), 6.90 (1H, s, cyclic-CH), 5.90 (1H, m, allyl-CH═), 5.3 (2H, m, allyl-CH_2═), 4.58 (2H, m, allyl-CH_2N), 3.9 (3H, s, CH_3), 3.88 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): 166.06 (CO-ester), 164.61 (C-4), 162.18 (CH═N), 156.69 (C-2), 141.01 (C-5), 137.86 (═CH(3)), 134.22 (Ar-C), 130 (Ar-C), 129.44 (allyl-CH═), 129.49, 127.06, 124.88, 123.93 (Ar-CH), 120.68 (═CH(2)), 118.12 (allyl-CH_2═), 115.12 (cyclic-CH), 54.77, 51.69 (CH_3), 44.58 (allyl-CH_2N). MS (EI): *m/z* (%) = 385 [M^+] (76), 354 (100), 278 (6), 211 (5), 174 (4), 144 (7), 128 (11), 83 (9), 59 (13), 44 (33). *Anal*. Calcd for $C_{19}H_{19}N_3O_4S$ (385.44): C, 59.21; H, 4.97; N, 10.90; S, 8.32. Found: C, 59.38; H, 5.08; N, 11.02; S, 8.23.

(Z)-Methyl 2-((Z)-2-{(E)-[(E)-2-methyl-3-phenylallylidene]-hydrazono}-4-oxo-3-phenylthiazol-idin-5-ylidene)acetate (13g). This compound was obtained as yellow crystals; mp 230–232°. IR (KBr): 1718 (C-4), 1700 (COO), 1605 (C-2) and 1600 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.1 (1H, $J = 9.8$, CH═N), 7.58–7.4

(10H, m, Ar-CH), 6.94 (1H, s, cyclic-CH), 6.80 (1H, s, CH attached to phenyl), 3.88 (3H, s, OCH_3), 2.55 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$): 166.08 (CO-ester), 165.54 (CH═N), 164.74 (C-4), 159.92 (C-2), 140.62 (C-5), 136.35, 134.89 (Ar-C), 133.92 (C-CH_3), 129.62, 129.34, 129.21, 128.42, 128.12, 127.64 (Ar-CH), 116.14 (cyclic-CH), 52.55 (OMe), 13.17 (CH_3). MS (EI): *m/z* (%) = 405 [M^+] (100), 377 (11), 346 (52), 328 (13), 261 (11), 142 (16), 119 (32), 103 (6), 59 (34), 44 (92). *Anal*. Calcd for $C_{22}H_{19}N_3O_3S$ (405.47): C, 65.17; H, 4.72; N, 10.36; S, 7.91. Found: C, 64.97; H, 4.83; N, 9.51; S, 7.56.

(Z)-Methyl-2-((Z)-2-{(E)-[(E)-hex-2-enyl-idene]hydrazono}-4-oxo-3-phenylthiazolidin-5-ylidene)acetate (13h). This compound was obtained as yellow crystals; mp 198-200°. IR (KBr): 1722 (C-4), 1695 (COO), 1645 (C-2) and 1608 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 7.9 (1H, d, *J* = 9.8, CH═N), 7.48–7.30 (5H, m, Ar-CH), 6.89 (1H, s, cyclic-CH), 6.30–6.15 (2H, m, CH═CH), 3.80 (3H, s, OCH_3), 2.15 (2H, m, CH_2), 1.4 (2H, m, CH_2), 0.85 (3H, t, *J* = 7.6, CH_3). ^{13}C NMR ($CDCl_3$): 166.31 (CO-ester), 164.71 (C-4), 162.49 (CH═N), 159.19 (C-2), 147.68 (═CH(3)), 141.49 (C-5), 133.33 (Ar-C), 129.29, 129.19, 127.87, 127.50 (Ar-CH and ═CH (2)), 116.44 (cyclic-CH), 52.52 (OMe), 35.09 (CH_2), 21.68 (CH_2), 13.66 (CH_3). MS (EI): *m/z* (%) = 357 [M^+] (26), 326 (4), 314 (100), 261 (5), 211 (8), 119 (9), 103 (6), 77 (12), 59 (8), 44 (16). *Anal*. Calcd for $C_{18}H_{19}N_3O_3S$ (357.43): C, 60.49; H, 5.36; N, 11.76; S, 8.97. Found: C, 60.31; H, 5.47; N, 11.65; S, 9.14.

(Z)-Methyl 2-((Z)-3-benzyl-2-{(E)-[(E)-hex-2-enylidene]-hydrazono}-4-oxothiazolidin-5-ylidene)acetate (13i). This compound was obtained as yellow crystals; mp 108°. IR (KBr): 1715 (C-4), 1700 (COO), 1648 (C-2) and 1608 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.02 (1H, d, *J* = 9.8, CH═N), 7.40 (2H, m, Ar-CH), 7.20 (3H, m, Ar-H), 6.83 (1H, s, cyclic-CH), 6.3 (2H, m, CH═CH), 5.02 (2H, s, CH_2-Ph), 3.78 (3H, s, OCH_3), 2.18 (2H, m, CH_2), 1.43 (2H, m, CH_2), 0.85 (3H, t, *J* = 7.6, CH_3). ^{13}C NMR ($CDCl_3$): 166.23 (CO-ester), 164.79 (C-4), 162.61 (CH═N), 158.77 (C-2), 147.81 (═CH(3)), 141.75 (C-5), 135.47 (Ar-C), 128.84, 128.10, 127.72 (Ar-CH), 116.3 (cyclic-CH), 52.43 (OMe), 46.79 (CH_2-Ph), 35.11 (CH_2), 21.70 (CH_2), 13.12 (CH_3). MS (EI): *m/z* (%) = 371 [M^+] (56), 343 (7), 328 (44), 302 (6), 261 (11), 119 (6), 103 (7), 91 (100), 65 (8), 59 (18), 44 (16). *Anal*. Calcd for $C_{19}H_{21}N_3O_3S$ (371.45): C, 61.44; H, 5.70; N, 11.31; S, 8.63. Found: C, 61.26; H, 5.81; N, 11.47; S, 8.50.

(Z)-Methyl 2-((Z)-3-allyl-2-{(E)-[(E)-hex-2-enylidene]-hydrazono}-4-oxothiazolidin-5-ylidene)acetate (13j). This compound was obtained as yellow crystals; mp 122°. IR (KBr): 1720 (CO), 1695 (COO), 1640 (C-2) and 1610 (Ar-C═C) cm^{-1}. NMR ($CDCl_3$): 8.0 (1H, d, *J* = 9.8, CH═N), 6.80 (1H, s, vinyl-CH), 6.25 (2H, m, CH═CH), 5.85 (1H, m, allyl-CH═), 5.20 (2H, m, allyl-CH_2═), 4.47 (2H, m, allyl-CH_2N), 3.80 (3H, s, OCH_3), 2.18 (2H, m, CH_2), 1.42 (2H, m, CH_2), 0.9 (3H, t, *J* = 7.6, CH_3). ^{13}C NMR ($CDCl_3$): 164.62 (CO-ester), 163.07 (C-4), 160.24 (CH═N), 158.39 (C-2), 145.09 (═CH(3)), 142.52 (C-5),128.65 (allyl-CH═), 126.11 (═CH(2)) 117.30 (allyl-CH_2═), 114.84 (vinyl-CH), 52.43 (OMe), 43.67 (allyl-CH_2N), 32.31 (CH_2), 20.13 (CH_2), 18.0 (CH_3). MS (EI): *m/z* (%) = 321 [M^+] (41), 293 (10), 278 (100), 252 (5), 211 (7), 83 (8), 59 (16), 44 (58). *Anal*. Calcd for $C_{15}H_{19}N_3O_3S$ (321.39): C, 56.06; H, 5.96; N, 13.07; S, 9.98. Found: C, 55.89; H, 6.09; N, 12.91; S, 10.13.

(Z)-Methyl 2-((Z)-2-{(E)-[(E)-but-2-enylidene]hydrazono}-4-oxo-3-phenylthiazolidin-5-ylidene)acetate (13k). This compound was obtained as yellow crystals; mp 210–212°. IR (KBr): 1718 (C-4), 1692 (COO), 1645 (C-2) and 1605 (Ar-C═C) cm^{-1}. ^1H NMR and ^{13}C NMR (see Table 2). MS (EI): *m/z* (%) = 329 [M^+] (52), 314 (100), 257 (6), 210 (10), 119 (8), 77 (9), 59 (8), 44 (16). $C_{16}H_{15}N_3O_3S$ (329.37): Calcd: C, 58.34; H, 4.59; N, 12.76; S, 9.74. Found: C, 58.19; H, 4.67; N, 12.91; S, 9.63.

(Z)-Methyl 2-((Z)-3-benzyl-2-{(E)-[(E)-but-2-enylidene]-hydrazono}-4-oxothiazolidin-5-ylidene)acetate (13l). This compound was obtained as yellow crystals; mp 149–150°. IR (KBr): 1718 (C-4), 1700 (COO), 1640 (C-2) and 1610 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.0 (1H, d, *J* = 9.8, CH═N), 7.40–7.2 (5H, m, Ar-CH), 6.80 (1H, s, cyclic-CH), 6.29 (2H, m, CH═CH), 5.04 (2H, s, CH_2-Ph), 3.80 (3H, s, OCH_3), 1.87 (3H, d, *J* = 6.55, CH_3). ^{13}C NMR ($CDCl_3$): 166.22 (CO-ester), 164.48 (C-4), 161.48 (CH═N), 158.12 (C-2), 142.66 (═CH(3)), 141.05 (C-5), 135.39 (Ar-C), 129.08, 128.83, 128.59 (Ar-CH), 128.10 (═CH(2)), 116.20 (cyclic-CH), 52.45 (OMe), 46.51 (CH_2-Ph). MS (EI): *m/z* (%) = 343 [M^+] (36), 328 (9), 273 (6), 261 (12), 130 (11), 119 (6), 91 (83), 65 (8), 59 (36), 44 (100). *Anal*. Calcd for $C_{17}H_{17}N_3O_3S$ (343.40): C, 59.46; H, 4.99; N, 12.24; S, 9.34. Found: C, 59.63; H, 5.07; N, 12.38; S, 9.19.

(Z)-Methyl 2-((Z)-3-allyl-2-{(E)-[(E)-but-2-enylidene]-hydrazono}-4-oxothiazolidin-5-ylidene)-acetate (13m). This compound was obtained as yellow crystals; mp 158–159°. IR (KBr): 1712 (CO), 1695 (COO), 1645 (C-2) and 1605 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 8.0 (1H, d, *J* = 9.94, CH═N), 6.82 (1H, s, cyclic-CH), 6.35–6.20 (2H, m, CH═CH), 5.8 (1H, m, allyl-CH═), 5.23–5.15 (2H, m, allyl-CH_2═), 4.47 (2H, m, allyl-CH_2N), 3.79 (3H, s, OCH_3), 1.89 (3H, d, *J* = 6.6, CH_3). ^{13}C NMR ($CDCl_3$): 166.92 (CO-ester), 164.67 (C-4), 161.92 (CH═N), 158.03 (C-2), 142.32 (═CH(3)), 141.26 (C-5), 129.02 (allyl-CH═), 130.22 (═CH (2)) 118.38 (allyl-CH_2═), 115.84 (cyclic-CH), 52.44 (OMe), 45.37 (allyl-CH_2N), 18.32 (CH_3). MS (EI): *m/z* (%) = 293 [M^+] (100), 278 (97), 262 (6), 225 (12), 211 (16), 170 (6), 83 (14), 59 (36), 44 (95). *Anal*. Calcd for $C_{13}H_{15}N_3O_3S$ (293.34): C, 53.23; H, 5.15; N, 14.32; S, 10.93. Found: C, 53.39; H, 5.06; N, 14.19; S, 11.11.

(Z)-Methyl 2-{(Z)-2-[(E)-(2-methylpropylidene)hydrazono]-4-oxo-3-phenylthiazolidin-5-ylidene}acetate (13n). This compound was obtained as yellow crystals; mp 182–184°. IR (KBr): 1722 (C-4), 1700 (COO), 1638 (C-2) and 1620 (Ar-C═C) cm^{-1}. NMR (CDCl3): 7.6 (1H, d, *J* = 9.8, CH═N), 7.45–7.30 (5H, m, Ar-CH), 6.9 (1H, s, vinyl-CH), 3.8 (3H, s, OCH_3), 2.55 (1H, m, CH), 1.05 (6H, *d*, J = 6.5, $2CH_3$). ^{13}C NMR ($CDCl_3$): 169.81 (CH═N), 166.06 (C-ester), 164.0 (C-4), 159.35 (C-2), 141.75 (C-5), 133.88 (Ar-C), 129.35, 129.05, 128.44 (Ar-CH), 116.12 (vinyl-CH), 52.52 (OMe), 31.90 (CH), 19.46 (CH_3). MS (EI): *m/z* (%) = 331 [M+] (68), 316 (24), 303 (25), 288 (9), 261 (38), 212 (10), 119 (33), 103 (8), 77 (13), 59 (35), 44 (100). *Anal*. Calcd for $C_{16}H_{17}N_3O_3S$ (331.39): C, 57.99; H, 5.17; N, 12.68; S, 9.68. Found: C, 58.14; H, 5.11; N, 12.53; S, 9.79.

(Z)-Methyl 2-{(Z)-3-benzyl-2-[(E)-(2-methylpropylidene)-hydrazono]-4-oxothiazolidin-5-ylidene}acetate (13o). This compound was obtained as yellow crystals; mp 119°. IR (KBr): 1715 (C-4), 1700 (COO), 1642 (C-2) and 1620 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 7.76 (1H, d, *J* = 9.8, CH═N), 7.40–7.20 (5H, m, Ar-CH), 6.80 (1H, s, cyclic-CH), 5.0 (2H, s, CH_2-Ph), 3.78 (3H, s, OCH_3), 2.6 (1H, m, CH), 1.08 (6H, d, *J* = 6.5, $2CH_3$). ^{13}C NMR ($CDCl_3$): 169.54 (CH═N), 166.40 (CO-ester), 165.07 (C-4), 158.39 (C-2), 142.03 (C-5), 133.29 (Ar-C), 128.87, 128.59, 128.02 (Ar-CH), 115.30 (cyclic-CH), 52.99 (OMe), 46.45 (CH_2-Ph), 37.89 (CH), 19.58 (CH_3). MS (EI): *m/z* (%) = 345 [M^+] (58), 302 (100), 275 (12), 212 (8), 133 (11), 117 (9), 91 (61), 65 (10), 59 (13), 44 (27). *Anal*. Calcd for $C_{17}H_{19}N_3O_3S$ (345.42): C, 59.11; H, 5.54; N, 12.17; S, 9.28. Found: C, 58.93; H, 5.48; N, 11.98; S, 9.39.

(Z)-Methyl 2-{(Z)-3-allyl-2-[(E)-(2-methylpropylidene)-hydrazono]-4-oxothiazolidin-5-ylidene}acetate (13p). This compound was obtained as yellow crystals; mp 149°. IR (KBr): 1720 (CO), 1690 (COO), 1640 (C-2) and 1615, 1590 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 7.73 (1H, d, $J = 9.8$, CH═N), 6.80 (1H, s, cyclic-CH), 5.85 (1H, m, allyl-CH═), 5.20 (2H, m, allyl-CH_2═), 4.42 (2H, m, allyl-CH_2N), 3.79 (3H, s, OCH_3), 2.55 (1H, m, CH), 1.1 (6H, d, $J = 6.5$, $2CH_3$). ^{13}C NMR ($CDCl_3$): 167.08 (CO-ester), 163.93 (C-4), 161.31 (CH═N), 158.62 (C-2), 139.58 (C-5), 127.74 (allyl-CH═), 116.12 (allyl-CH_2═), 113.35 (cyclic-CH), 50.07 (OMe), 42.77 (allyl-CH_2N), 29.46 (CH), 17.63 (CH_3). MS (EI): *m/z* (%) = 295 [M^+] (61), 280 (12), 252 (100), 225 (34), 212 (44), 116 (12), 83 (17), 59 (9), 41 (35). *Anal*. Calcd for $C_{13}H_{17}N_3O_3S$ (295.36): C, 52.86; H, 5.80; N, 14.23; S, 10.86. Found: C, 53.03; H, 5.71; N, 14.06; S, 11.05.

(Z)-Methyl 2-{(Z)-2-[(E)-(2-methylbutylidene)hydrazono]-4-oxo-3-phenylthiazolidin-5-ylidene}acetate (13q). This compound was obtained as yellow crystals; mp 172–174°. IR (KBr): 1722 (C-4), 1700 (COO), 1640 (C-2) and 1590 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 7.65 (1H, d, $J = 9.8$, CH═N), 7.53–7.40 (5H, m, Ar-CH), 6.94 (1H, s, cyclic-CH), 3.9 (3H, s, OCH_3), 2.38 (1H, m, CH), 1.38 (2H, m, CH_2), 1.1 (3H, d, $J = 6.5$, CH_3), 0.9 (3H, t, $J = 7.68$, CH_3). ^{13}C NMR ($CDCl_3$): 168.57 (CH═N), 165.59 (CO-ester), 163.91 (C-4), 158.63 (C-2), 140.90 (C-5), 132.91 (Ar-C), 128.46, 128.29, 126.12 (Ar-CH), 11.20 (cyclic-CH), 52.52 (OMe), 37.69 (CH), 26.31 (CH_2), 16.31 (CH_3), 10 (CH_3). MS (EI): *m/z* (%) = 345 [M^+] (44), 330 (32), 303 (61), 261 (22), 247 (6), 119 (16), 103 (8), 77 (12), 59 (40), 44 (100). *Anal*. Calcd for $C_{17}H_{19}N_3O_3S$ (345.42): C, 59.11; H, 5.54; N, 12.17; S, 9.28. Found: C, 58.96; H, 5.61; N, 11.99; S, 9.41.

(Z)-Methyl 2-{(Z)-2-[(E)-decylidenehydrazono]-4-oxo-3-phenylthiazolidin-5-ylidene}acetate (13r). This compound was obtained as yellow crystals; mp 132°. IR (KBr): 1728 (C-4), 1700 (COO), 1642 (C-2) and 1620, 1590 (Ar-C═C) cm^{-1}. ^1H NMR ($CDCl_3$): 7.70 (1H, d, $J = 9.8$, CH═N), 7.45–7.30 (5H, m, Ar-CH), 6.90 (1H, s, cyclic-CH), 3.8 (3H, s, OCH_3), 2.3 (2H, m, CH_2), 1.50 (2H, m, CH_2), 1.19 (12H, m, CH_2), 0.8 (3H, t, $J = 7.6$, CH_3). ^{13}C NMR ($CDCl_3$): 166.59 (CH═N), 165.66 (CO-ester), 164.58 (C-4), 159.05 (C-2), 141.66 (C-5), 129.26, 128.06, 127.35 (Ar-CH), 116.56 (cyclic-CH), 52.50 (OMe), 32.38, 31.88, 29.88, 29.38, 29.29, 29.01, 26.12, 22.52 (CH_2), 14.12 (CH_3). MS (EI): *m/z* (%) = 415 [M^+] (59), 330 (8), 303 (100), 261 (12), 119 (10), 77 (7), 59 (16), 44 (58). *Anal*. Calcd for $C_{22}H_{29}N_3O_3S$ (415.55): C, 63.59; H, 7.03; N, 10.11; S, 7.72. Found: C, 63.73; H, 6.94; N, 9.92; S, 7.87.

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REFERENCES AND NOTES

[1] Aly, A. A.; Hassan, A. A.; El-Sheref, E. M.; Mohamed, M. A.; Brown, A. B. J Heterocycl Chem 2008, 45, 521.

[2] Fodor, L.; Bernäth, G.; Sohár, P.; Gröschl, D.; Meier, H. Monatsh Chem 2006, 137, 231.

[3] Csomös, P.; Fodor, L.; Bernäth, G.; Sinkkonen, J.; Salminen, J.; Wiinamäki, K.; Pihlaja, K. Tetrahedron 2008, 64, 1002.

[4] Yadav, J. S.; Reddy, B. V. S.; Yadav, N. N.; Gupta, M. K. Tetrahedron Lett 2008, 49, 2815.

[5] Darehkordi, A.; Saidi, K.; Islami, M. R. Arkivoc 2007, (i), 180.

[6] Terzidis, M. A.; Stephanidou-Stephanatou, J.; Tsoleridis, C. A. Tetrahedron Lett 2009, 50, 1196.

[7] Fabian, B.; Csámpai, A.; Nagy, T. Z. S.; Czugler, M.; Sohár, P. J Organomet Chem 2009, 694, 3732.

[8] Tozkoparan, B.; Aktay, G.; Yesilada, E. Farmaco 2002, 57, 145.

[9] Schmeyers, J.; Kaupp, G. Tetrahedron 2002, 58, 7241.

[10] Fäbian, B.; Kudar, V.; Csämpai, A.; Nagy, T. Z. S.; Sohár, P. J Organomet Chem 2007, 692, 5621.

[11] Berseneva, V. S.; Tkachev, A. V.; Morzherin, Y. Y.; Dehaen, W.; Luyten, I.; Toppet, S.; Bakulev, V. A. J Chem Soc Perkin Trans 1 1998, 2133.

[12] Hassan, A. A.; Ibrahim, Y. R.; Shawky, A. M. J Chem Res 2008, 72.

[13] Hassan, A. A.; Shehata, H. S.; Döpp, D. J Chem Res 2008, 725.

[14] Lee, C. L.; Sim, M. M. Tetrahedron Lett 2000, 41, 5729.

[15] Andres, C. J.; Bronson, J. J.; D'Andrea, S. V.; Deshpande, M. S.; Falk, P. T.; Grant-Young, K. A.; Harte, W. E.; Ho, H.-T.; Misco, P. F.; Robertson, J. G.; Stock, D.; Sun, Y.; Walsh, A. W. Bioorg Med Chem Lett 2000, 10, 715.

[16] Castro, A.; Encinas, A.; Gil, C.; Bräse, S.; Porcal, W.; Pérez, C.; Morero, F. J.; Martinez, A. Bioorg Med Chem 2008, 16, 495.

[17] Abdel-Ghani, E. J Chem Res, Synop 1999, 174.

[18] Soltero-Higgin, M.; Carlson, E. E.; Phillips, J. H.; Kiessling, L. L. J Am Chem Soc 2004, 126, 10532.

[19] Andreani, A.; Rambaldi, M.; Leoni, A.; Locatelli, A.; Bossa, R.; Chiericozzi, M.; Galatulas, I.; Salvatore, G. Eur J Med Chem 1996, 31, 383.

[20] Liu, W.; Bulgaru, A.; Haigentz, M.; Stein, C. A.; Perez-Soler, R.; Mani, S. Curr Med Chem Anti Canc Agents 2003, 3, 217.

[21] Lugovskoy, A. A.; Degterev, A. I.; Fahmy, A. F.; Zhou, P.; Gross, J. D.; Yuan, J.; Wagner, G. J Am Chem Soc 2002, 124, 1234.

[22] Chen, H.; Fan, Y.-H.; Natarajan, A.; Guo, Y.; Iyasere, J.; Harbinski, F.; Luus, L.; Christ, W.; Aktas, H.; Halperin, J. A. Bioorg Med Chem Lett 2004, 14, 5401.

[23] Sohár, P. Nuclear Magnetic Resonance Spectroscopy; CRC Press: Boca Raton, FL, 1983; Vol 2, p 89.

[24] (a) Vögeli, U.; von Philipsborn, W.; Nagarajan, K.; Nair, M. D. Helv Chim Acta 1978, 61, 607. (b) Danilkina, N. A.; Mikhailov, L. E.; Ivin, B. A. Russ J Org Chem 2006, 42, 783.

[25] Breitmaier, E.; Voelter, W. Carbon-13 NMR Spectroscopy, 3rd ed.; VCH: Weinheim, 1987; pp 134–147. Pretsch, E.; Bühlmann, P.; Badertscher, M. Structure Determination of Organic Compounds, 4th ed.; Springer: Berlin, 2009; pp 80–84, 93–100.

[26] Abraham, R. J.; Fisher, J.; Loftus, P. Introduction to NMR Spectroscopy; John Wiley & Sons: Chichester, 1988; pp 72–80.

[27] Shah, I. D.; Trivedi, J. P. J Indian Chem Soc 1963, 40, 889.

[28] Pulvermacher, G. Ber Dtsch Chem Ges 1894, 27, 613.

[29] Cunha, S.; Lima da Silva, T. Tetrahedron Lett 2009, 50, 2090.

[30] Grammaticakis, P. Bull Soc Chim Fr 1950, 504; 1953, 86.

[31] Walter, W.; Rohloff, C. Justus Liebigs Ann Chem 1977, 447.