Syntheses of 4-(5-oxo-1,2,4-triazol-3-yl)-sydnones and 4-(4-arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones from Sydnone Derivatives and Their Fragments

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4-(5-oxo-1,2,4-triazol-3-yl)-sydnones **11** and 4-(4-arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones **13** have been obtained from a-chloroformylarylhydrazine hydrochloride **2**. Moreover, the intermediates, including **3**, **4**, **9** and **10,** in this study are synthetically informative and valuable. It is also noteworthy that three reactants, **1**, **2** and sydnonecarbaldehydes, were prepared from sydnone derivatives and their fragments. The oxidative cyclizations of sydnonecarbaldehyde semicarbazones **9** and carbazones **10** with two different oxidizing agents ($Cu(ClO_4)_2$ and $Fe(ClO_4)_3$) have been extensively examined. The reaction time and the yields of cyclizations were affected by the substituents of semicarbazones **9** and carbazones **10**.

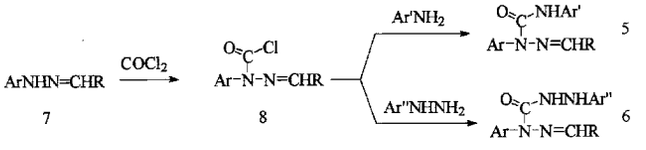
INTRODUCTION

1,2,4-triazol-3-ones and its derivatives, 4-amino-1,2,4-triazol-3-one, possess special pharmacological activities.[1-4] Some sydnone compounds also show biological and pharmacological activities.[5-11] In addition, synthetic reactions using sydnones are experimentally demanding as these compounds are unstable toward both acidic and basic media, Hence the syntheses must be carried out with careful consideration of temperature, reaction path and reagents etc.[5] 3-Arylsydnones and 3-aryl-4-chlorosydnones in acidic conditions result in a ring opening to produce arylhydrazine hydrohalide **1**[12-20] and α-chloroformylarylhydrazine hydrohalide **2**,[21] respectively, and they are valuable reagents for the synthesis of heterocyclic compounds.[21,22] Therefore, synthetic studies using these decomposition products of sydnones with sydnone derivatives to synthesize heterocyclic compound at 4-position of sydnones are of great interest.

Semicarbazides and carbazides, in this report, were the precursors of 4-heterocyclic substituted sydnones and various improved synthetic routes developed for substituted semicarbazides and carbazides have been reported.[23-29] We modified the previous experiment[21] to prepare 2,4-diarylsemicarbazides **3** by the reaction of α-chloroformylarylhydrazine hydrohalide **2** with arylamine in EtOAc at room temperature. We have also extended this synthetic method to give carbarzides **4** by hydrazines steated of arylamine reacted with compound **2** and the product, 1,4-diarylcarbazides **4**, possessing substituents at 1,4-positions, which were rarely found in literature.

Generally, 2,4-diarylsemicarbazones **5** and 2,5-diarylcarbazones **6** were prepared by arylhydrazone **7** reacting with phosgene to give α-chloroformylhydrazone **8** which would react with arylamine to give 2,4-diarylsemicarbazones **5** [1,22,30-31] or react with arylhydrazine to give 2,5-diarylcarbazones **6** [22](Scheme I). However, the reagent, phosgene, is expensive and dangerous contraband and the reaction must be heated and dehydrated. Besides, 2,4-diarylsemicarbazones **5** were also obtained by arylhydrazones **7** reacting with isocyanic acid aryl ester[1,25,33-34] at the expense of a long reaction time and an excess amount of isocyanic acid aryl ester. Hence compounds **9** and **10** were performed by employed compounds **3** and **4** reacted with compounds **2** would be suitable route.

Scheme I



Furthermore, the cyclization reactions of sydnonecarbaldehyde semicarbazones **9** would proceed to give compounds **11** by various oxidizing reagents,[1,30] such as $FeCl_3$, PbO_2 and $CsCO_3$, which have been employed for the cyclization of aldehyde semicarbazone, failed for compounds **9** transfer to compounds **11**, and resulted in fragmentation of starting materials especially in $CsCO_3$ case. After a sequence of various oxidizing studies, $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ were suitable agents[32] for the cyclization of compounds **9**. Further work on the cyclic reaction of compounds **10**, using

Dedicated to the memory of the late Professor Ta-shue Chou

Table 1. Preparation of Compounds **1a ~ 1g** from 3-Arylsydnones

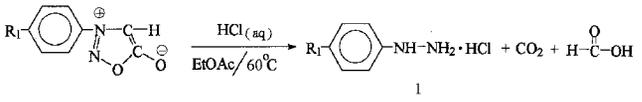
Compound	R_1	Yield %	M.P.(°C)	M.P.(°C,Liter.)
1a	H	79	240-241	241-244
1b	CH_3	76	233-233.5	222-235
1c	C_2H_5O	87	165.5-166.5	165
1d	Cl	90	223-224	225-226
1e	F	88	216(dec.)	216(dec.)
1f	C_2H_5OCO	79	220-221	220-221
1g	NO_2	75	201-202	201-202

$Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ as oxidizing cyclic reagents[1,30] provided no expected product of 1,2,4,5-tetrazin-3-ones **12**, but 4-arylamino-1,2,4-triazol-3-ones **13** were produced. This result offer a new route to obtain 4-arylamino-1,2,4-triazol-3-one compounds from carbarzones through oxidization of $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$.

RESULTS AND DISCUSSION

α-Chloroformylarylhydrazine hydrochlorides **2** were obtained by decomposition of 3-aryl-4-chlorosydnones[21] in EtOAc as solvent and arylhydrazine hydrochlorides **1** were obtained by decomposition of 3-arylsydnones in acidic water. We modified this synthetic method by using EtOAc as solvent (Scheme II), instead of the above described water, to facilitate the synthetic work (Table 1).

Scheme II



Since Compounds **1** and **2** were acquired easily from sydnone compounds, preparation of carbazides **4** (Table 2) by the reaction of α-chloroformylarylhydrazine hydrochloride **2** with arylhydrazine hydrochloride **1** (Scheme III) proved better than other published methods.[26-29] Similarly, semicarbazides **3** were also acquired (Table 3) by the reaction of compounds **2** reacted with arylamine in EtOAc at room temperature (Scheme III). The yields of these reactions were dependent on the electronic effects of the substituents borne by the arylamine, the ability of N-acylation increased by π–donating group (CH_3O-), and decreased by π–withdrawing group (EtOCO-). Contrary to above results, the yields of carbarzides **4** were independent on the substituents borne by the arylhydrazines. The lower yields (Table 2) may be N-1 would rather base than nucleophile to acylation and resulted in self-dimerization of compounds **2**.

Scheme III

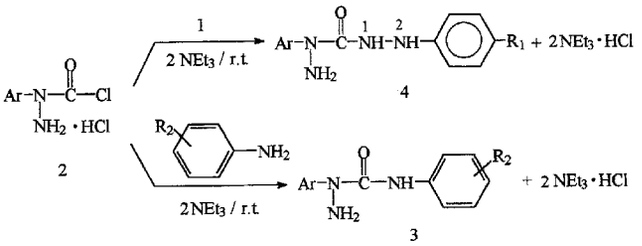


Table 2. Preparation of Compounds **4a ~ 4l** from Compounds **1** and **2**

Compound	Ar	R_1	Yield %
4a	p-$CH_3C_6H_4$	H	45
4b	p-ClC_6H_4	H	40
4c	p-ClC_6H_4	CH_3	48
4d	C_6H_5	C_2H_5O	46
4e	p-$CH_3C_6H_4$	C_2H_5O	37
4f	p-$CH_3C_6H_4$	Cl	35
4g	C_6H_5	F	47
4h	p-$CH_3C_6H_4$	F	45
4i	p-ClC_6H_4	F	42
4j	p-$CH_3OC_6H_4$	F	45
4k	p-$CH_3C_6H_4$	C_2H_5OCO	57
4l	p-ClC_6H_4	C_2H_5OCO	50

Table 3. Preparation of Compounds **3a~ 3g** from Compound **1**

Compound	Ar	R_2	Yield %
3a	p-$CH_3OC_6H_4$	p-CH_3O	75
3b	C_6H_5	p-CH_3	72
3c	p-$CH_3C_6H_4$	H	70
3d	p-ClC_6H_4	p-Cl	58
3e	p-ClC_6H_4	p-F	35
3f	C_6H_5	m-Cl	43
3g	p-$CH_3C_6H_4$	p-C_2H_5OCO	32

Aldehyde carbazones and semicarbazones are the precursors of several heterocyclic compounds. Instead of utilizing the reported methods,[22,30-31] we made use of the chemical reactivity of sydnones to prepare compounds **9** and **10** as dem-

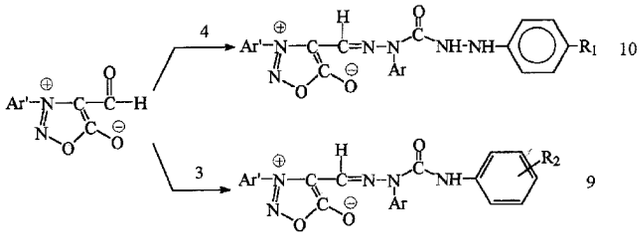
Table 4. Preparation of Compounds **9a ~ 9g** from Compound **3**

Compound*	Ar	R_2	Yield %
9a	p-$CH_3OC_6H_4$	p-CH_3O	91
9b	C_6H_5	p-CH_3	90
9c	p-$CH_3C_6H_4$	H	90
9d	p-ClC_6H_4	p-Cl	88
9e	p-ClC_6H_4	p-F	83
9f	C_6H_5	m-Cl	87
9g	p-$CH_3C_6H_4$	p-C_2H_5OCO	89

*: Ar' = p-$CH_3OC_6H_4$-

onstrated by Scheme IV. In the study, sydnonecarbaldehyde semicarbazones **9** (Table 4) and carbazones **10** (Table 5) containing mesoionic rings are obtained in a simple , mild condition and yet with high yields.

Scheme IV



In a separate study at this lab, the cyclization of aldehyde carbazones could proceed in acidic and heat conditions, whereas cyclizations of either sydnonecarbaldehyde semicarbazone **9** or carbazones **10** failed under the same conditions. This can be explained by the higher charge density on the carbon of C=N due to the greater electron-releasing property of the sydnone ring carbon atom than that of general aldehydes. In order to reach our final goal, the syntheses of 4-heterocyclic substituent sydnones, several oxidizing cyclic reagents were used in this synthetic work. $FeCl_3$, PbO_2 and $CsCO_3$ failed for cyclization of compounds **9** and **10**, only the starting material was recollected in first two reagents and $CsCO_3$ resulted in decomposition of the starting material.

Gruttadauria[32] had employed $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ to perform the cyclization of semicarbazones and described the cyclic mechanism of semicarbazones due to electrophilic attack of a nitrogen cation on the C=N double bond. This conclusion was also valid in the cyclization of compounds **9** succeed, because C=N double bond of compounds **9** possess high charge density resulting from the electron-releasing property of sydnone ring carbon atom and attack enough nitrogen cation.

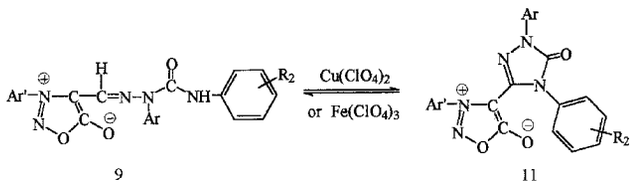
Table 5. Preparation of Compounds **10a** ~ **10k** from Compound **4**

Compound*	Ar	R_1	Yield %
10a	p-$CH_3C_6H_4$	H	85
10b	p-ClC_6H_4	H	87
10c	p-ClC_6H_4	CH_3	87
10d	C_6H_5	C_2H_5O	83
10e	p-$CH_3C_6H_4$	C_2H_5O	93
10f	p-$CH_3C_6H_4$	Cl	86
10g	C_6H_5	F	91
10h	p-$CH_3C_6H_4$	F	90
10i	p-$CH_3OC_6H_4$	F	92
10j	p-$CH_3C_6H_4$	C_2H_5OCO	87
10k	p-ClC_6H_4	C_2H_5OCO	94

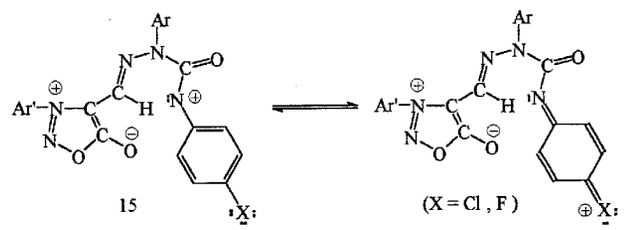
*: Ar' = p-$CH_3C_6H_4$-

The cyclizations of compounds **9** to gain 4-(5-oxo-1, 2,4-triazol-3-yl)-sydnones **11** using $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ had different reaction results (Scheme V). As $Cu(ClO_4)_2$ was utilized, the yield was sensitive to the subsitituent R_2. It is evident that electron-donating groups, (**11a,11b**), resulted in higher yields than electron-withdrawing groups (Table 6). Using $Fe(ClO_4)_3$ as oxidizing agent; on the other hand, the reaction took place with high yields (Table 6) when R_2 are electron-donating groups. However, while R_2 are para-hydrogen (**11c**), meta-chloride (**11f**) or para-ethoxycarbonyl group (**11g**), the reactions did not proceed at all. For halides, such as chloride or fluoride at para position, the reaction took place even though they are σ-withdrawing groups. This is well understood since the halides at the para position may donate electrons through a mesomeric effect to stabilize nitrogen cation of the intermediate **15** (Scheme VI). In other words, our results provide evidence in support of the mechanism proposed by M.Gruttadauria et al..[32]

Scheme V



Scheme VI



Because N-2 possessing higher charge density transfer to more stable nitrogen cation than N-1, according to above reaction mechanism, the oxidizing cyclizations of sydnonecarbaldehyde carbazones **10** to gain 4-(6-oxo-1,2,4,5-tetrazin-3-yl)-sydnones **12** by $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ were our original expectation (Scheme VII). Surprisingly, N-1 nitrogen cation was formed in cyclization of compounds **10** and 4-(4-arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones **13** were obtained by structure identification of X-ray spectra (Fig.1, Table 8 ~ 11). The oxidizing cyclizations of compounds **10** transferred to 4-(4-arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones **13** were virtually identical in view of reaction re-

Table 6. Preparation of Compounds **11a ~ 11g** from Compounds **9**

Compound*	Ar	R_2	$Cu(ClO_4)_2$		$Fe(ClO_4)_3$	
			Time	Yield %	Time	Yield %
11a	p-$CH_3OC_6H_4$	p-CH_3O	20 min	73	20 min	72
11b	C_6H_5	p-CH_3	2 hr	70	2 hr	71
11c	p-$CH_3C_6H_4$	H	4 hr	-	4 hr	-
11d	p-ClC_6H_4	p-Cl	4 hr	50	4 hr	50
11e	p-ClC_6H_4	p-F	4 hr	52	4 hr	51
11f	C_6H_5	m-Cl	4 hr	46	4 hr	-
11g	p-$CH_3C_6H_4$	p-EtOCO	4 hr	48	4 hr	-

*: Ar' = p-$CH_3OC_6H_4$-

Table 7. Preparation of Compounds **13a ~ 13j** from **10** with Oxidizing Agents

Compound*	Ar	R_1	$Cu(ClO_4)_2$		$Fe(ClO_4)_3$	
			Molar rate	Yield%	Molar rate	Yield %
13a	p-$CH_3C_6H_4$	H	2 eq	61	2 eq	63
13b	p-ClC_6H_4	H	2 eq	58	2 eq	57
13c	p-ClC_6H_4	CH_3	2 eq	60	2 eq	61
13d	p-$CH_3C_6H_4$	EtO	1.1 eq	20	1.1 eq	18
13e	p-$CH_3C_6H_4$	Cl	2 eq	65	3 eq	70
13f	C_6H_5	F	2 eq	68	3 eq	68
13g	p-$CH_3C_6H_4$	F	2 eq	65	3 eq	60
13h	p-$CH_3OC_6H_4$	F	2 eq	65	3 eq	63
13i	p-$CH_3C_6H_4$	EtOCO	2 eq	67	4 eq	62
13j	p-ClC_6H_4	EtOCO	2 eq	63	4 eq	65

*: Ar' = p-$CH_3C_6H_4$-, the reaction temperature of 13d is 45 °C, the others are 80 °C.

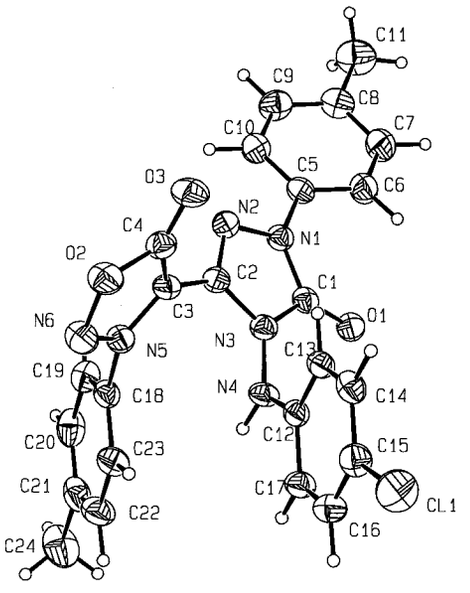


Fig. 1. Molecular structure of 4-(4-(4-chlorophenyl-amino)-1-(4-(methyl-phenyl)-5-oxo-4,5-di-hydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphe nyl)sydnone (**13e**).

sults and yield percentages (Scheme VII, Table 7). The molar ratio of $Cu(ClO_4)_2$ / **13** required is independent of the substituent R_1, while the molar ratio of $Fe(ClO_4)_3$ / **13** required would vary with R_1. In general, the stronger the electron-withdrawing effect is, the higher the quantity of oxidizing agent needed. For compound **13d**, the yield was much lower than those of the other substituents. The reason is that fierce reactions result in either decomposition of the starting material (**10e**) which gives sydnonecarbaldehyde hydrazone or side reactions to produce unknown compounds (even though the reaction temperature was lowered from 80 °C to 0

Scheme VII

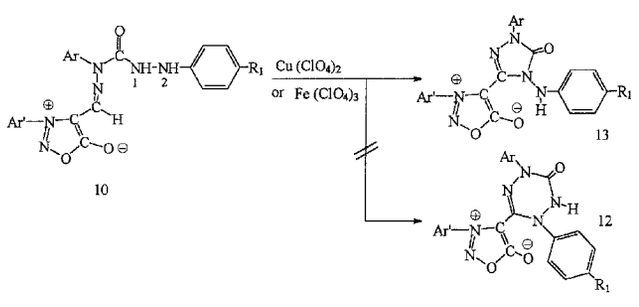


Table 8. Crystal Data of **13e**

Formula	$C_{24}H_{19}ClN_6O_3$
Formula weight	474.91
Cryst system	Triclinic
Space group	P-1
a / Å	8.4019 (19)
b / Å	10.7399 (12)
c / Å	13.2314 (21)
α	99.79 (4)
β	97.935 (17)
γ	100.24 (5)
V / Å^3	1140.3 (3)
Z	2
D_c / g cm^3	1.348
F_{000}	479.89
λ (Mo-Kα) Å	0.70930
μ/ cm^{-1}	0.20
Range / deg	19.44-26.06
Scan type	2θ
$2\theta_{max}$	49.8
Reflections measured	4288
Unique reflections	3989
Observed reflections	3044
Refined parameters	308
R_f for significant reflections	0.042
R_w for significant reflections	0.045
GoF	2.05

Table 9. Bond Distances / Å of **13e**

Cl(1)-C(15)	1.742(3)	C(13)-C(14)	1.382(3)
C(1)-N(1)	1.367(3)	C(13)-H(13)	1.00
C(1)-N(3)	1.384(3)	C(14)-C(15)	1.376(4)
C(1)-O(1)	1.222(3)	C(14)-H(14)	0.99
C(2)-C(3)	1.447(3)	C(15)-C(16)	1.376(4)
C(2)-N(2)	1.296(3)	C(16)-C(17)	1.375(4)
C(2)-N(3)	1.372(3)	C(16)-H(16)	0.99
C(3)-C(4)	1.409(3)	C(17)-H(17)	0.98
C(3)-N(5)	1.351(3)	C(18)-C(19)	1.372(3)
C(4)-O(2)	1.425(3)	C(18)-C(23)	1.372(3)
C(4)-O(3)	1.202(3)	C(18)-N(5)	1.447(3)
C(5)-C(6)	1.374(3)	C(19)-C(20)	1.389(4)
C(5)-C(10)	1.377(3)	C(19)-H(19)	1.01
C(5)-N(1)	1.429(3)	C(20)-C(21)	1.385(5)
C(6)-C(7)	1.383(4)	C(20)-H(20)	1.00
C(6)-H(6)	0.98	C(21)-C(22)	1.376(4)
C(7)-C(8)	1.374(4)	C(21)-C(24)	1.509(4)
C(7)-H(7)	1.00	C(22)-C(23)	1.374(3)
C(8)-C(9)	1.387(4)	C(22)-H(22)	1.01
C(8)-C(11)	1.509(4)	C(23)-H(23)	0.98
C(9)-C(10)	1.379(4)	C(24)-H(24a)	0.96
C(9)-H(9)	0.98	C(24)-H(24b)	0.96
C(10)-H(10)	1.00	C(24)-H(24c)	0.96
C(11)-H(11a)	0.99	N(1)-N(2)	1.381(3)
C(11)-H(11b)	0.99	N(3)-N(4)	1.3812(25)
C(11)-H(11c)	0.98	N(4)-H(N4)	0.96
C(12)-C(13)	1.383(3)	N(5)-N(6)	1.308(3)
C(12)-C(17)	1.397(3)	N(6)-O(2)	1.377(3)
C(12)-N(4)	1.402(3)		

°C). After a sequence of various temperature studies (10 °C / step), the best yield was 20% as the reaction proceeded at 45 °C.

CONCLUSION

Four potent precursors of hereocyclic compounds, **3**,**4**,**9** and **10** were prepared easily by sydnone derivatives and their fragments. On the way of cyclic reactions, these result suggest that oxidative cyclization of compounds **9** to gain compounds **11**, $Cu(ClO_4)_2$ was the better oxidizing agent than $Fe(ClO_4)_3$. However, as R_2 is hydrogen atom, the reaction was not proceeded whichever reagent was adopted. Contrarily, compounds **10** transferred to compounds **13**, both reagents were practicable except R_1 is resonance donation group. Pharmaceutical tests of two heterocyclic compounds, compounds **11** and **13**, are underway. The developed synthetic route for 4-arylamino-1,2,4-triazol-3-ones **13** from carbazones **10** is different from traditional methods.[33-36]

EXPERIMENTAL SECTION

General

Melting points (Buchi 535 apparatus) are uncorrected. IR spectra were recorded on a Hitachi 270-30 infrared spectrometer. NMR spectra were measured on a Bruker AMX-200 NMR spectrometer with tetramethylsilane as internal standard. The mass spectra were registered on a Finnigan MAT TSQ-46C spectrometer at an ionizing potential 70 eV. Elemental analyses were performed on Heraeus CHN-O-Rapid and Tacussel Coulomax 78 analyzers. X-ray analysis was made with a Nonius CAD-4 diffractometer. Column chromatography was carried out on silica gel (Kieselgel 100, 230-400 mesh, E. Merck)

Preparation of Arylhydrazine Hydrochlorides 1a ~1g

A solution of 3-phenylsydnone (10 g, 61.7 mmol) in EtOAc (100 mL) and $HCl_{(aq)}$ (12M, 12 mL) was heated at 60 °C for 15 min. After cooling, the solid product was separated by filtration, then washed with cold EtOAc and dried in vacuum to afford phenyldrazine hydrochloride **1a** (7.05 g, 79%).

Phenylhydrazine hydrochloride (1a)

Pale brown powder; mp 240~241 °C, IR (KBr), cm^{-1}: 3208 (νN-H), 3160~2764 [(-NH_3^+)νN-H], ^{1}H NMR (DMSO-d_6), δ = 10.26 (br, 3H), 7.30~7.22 (m, 2H), 7.00~6.88 (m, 3H), EIMS (70eV), *m/z* (%): 108 (M^+-36, 100), 92 (68), 77 (42), 65 (68). Anal.Calcd. for $C_6H_9N_2Cl$ (144.61): C: 49.84, H: 6.27,

Table 10. Bond Angles/deg of **13e**

N(1)-C(1)-N(3)	102.46(18)	C(14)-C(15)-C(16)	120.86(23)
N(1)-C(1)-O(1)	129.76(20)	C(15)-C(16)-C(17)	119.73(22)
N(3)-C(1)-O(1)	127.76(20)	C(15)-C(16)-H(16)	120.2
C(3)-C(2)-N(2)	123.78(19)	C(17)-C(16)-H(16)	120.1
C(3)-C(2)-N(3)	124.38(19)	C(12)-C(17)-C(16)	119.97(21)
N(2)-C(2)-N(3)	111.23(19)	C(12)-C(17)-H(17)	119.4
C(2)-C(3)-C(4)	126.69(20)	C(16)-C(17)-H(17)	120.6
C(2)-C(3)-N(5)	126.39(19)	C(19)-C(18)-C(23)	122.15(21)
C(4)-C(3)-N(5)	106.58(19)	C(19)-C(18)-N(5)	118.74(20)
C(3)-C(4)-O(2)	103.08(19)	C(23)-C(18)-N(5)	119.05(20)
C(3)-C(4)-O(3)	136.75(23)	C(18)-C(19)-C(20)	117.95(24)
O(2)-C(4)-O(3)	120.17(20)	C(18)-C(19)-H(19)	120.2
C(6)-C(5)-C(10)	120.53(21)	C(20)-C(19)-H(19)	121.7
C(6)-C(5)-N(1)	120.17(21)	C(19)-C(20)-C(21)	121.09(24)
C(10)-C(5)-N(1)	119.29(20)	C(19)-C(20)-H(20)	118.4
C(5)-C(6)-C(7)	119.10(24)	C(21)-C(20)-H(20)	120.5
C(5)-C(6)-H(6)	120.2	C(20)-C(21)-C(22)	118.78(23)
C(7)-C(6)-H(6)	120.6	C(20)-C(21)-C(24)	120.2(3)
C(6)-C(7)-C(8)	122.05(25)	C(22)-C(21)-C(24)	121.0(3)
C(6)-C(7)-H(7)	119.5	C(21)-C(22)-C(23)	121.22(25)
C(8)-C(7)-H(7)	118.5	C(21)-C(22)-H(22)	119.4
C(7)-C(8)-C(9)	117.44(23)	C(23)-C(22)-H(22)	119.4
C(7)-C(8)-C(11)	121.8(3)	C(18)-C(23)-C(22)	118.80(23)
C(9)-C(8)-C(11)	120.8(3)	C(18)-C(23)-H(23)	120.3
C(8)-C(9)-C(10)	121.74(24)	C(22)-C(23)-H(23)	120.8
C(8)-C(9)-H(9)	118.8	C(21)-C(24)-H(24a)	111.9
C(10)-C(9)-H(9)	119.5	C(21)-C(24)-H(24b)	111.5
C(5)-C(10)-C(9)	119.16(23)	C(21)-C(24)-H(24c)	111.6
C(5)-C(10)-H(10)	120.2	H(24a)-C(24)-H(24b)	107.3
C(9)-C(10)-H(10)	120.6	H(24a)-C(24)-H(24c)	107.5
C(8)-C(11)-H(11a)	110.6	H(24b)-C(24)-H(24c)	106.9
C(8)-C(11)-H(11b)	111.6	C(1)-N(1)-C(5)	127.16(18)
C(8)-C(11)-H(11c)	112.0	C(1)-N(1)-N(2)	112.80(17)
H(11a)-C(11)-H(11b)	106.8	C(5)-N(1)-N(2)	119.94(17)
H(11a)-C(11)-H(11c)	107.7	C(2)-N(2)-N(1)	104.71(17)
H(11b)-C(11)-H(11c)	107.9	C(1)-N(3)-C(2)	108.79(18)
C(13)-C(12)-C(17)	119.74(20)	C(1)-N(3)-N(4)	125.59(17)
C(13)-C(12)-N(4)	122.97(19)	C(2)-N(3)-N(4)	125.22(18)
C(17)-C(12)-N(4)	117.18(19)	C(12)-N(4)-N(3)	119.40(16)
C(12)-C(13)-C(14)	119.85(20)	C(12)-N(4)-H(N4)	120.0
C(12)-C(13)-H(13)	119.7	N(3)-N(4)-H(N4)	120.5
C(14)-C(13)-H(13)	120.4	C(3)-N(5)-C(18)	128.60(18)
C(13)-C(14)-C(15)	119.85(21)	C(3)-N(5)-N(6)	114.95(18)
C(13)-C(14)-H(14)	120.0	C(18)-N(5)-N(6)	116.43(17)
C(15)-C(14)-H(14)	120.1	N(5)-N(6)-O(2)	104.22(17)
Cl(1)-C(15)-C(14)	119.27(20)	C(4)-O(2)-N(6)	111.14(16)
Cl(1)-C(15)-C(16)	119.87(20)		

Table 11. Atomic Coordinates of **13e**

Atom	X	Y	Z	Bios
Cl(1)	0.06530(10)	0.21958(9)	0.03387(6)	7.51(5)
C(1)	0.5157(3)	0.19268(20)	0.56096(17)	3.76(10)
C(2)	0.6927(3)	0.32981(20)	0.49907(17)	3.77(10)
C(3)	0.7675(3)	0.39479(20)	0.42489(16)	3.89(9)
C(4)	0.7537(3)	0.51802(21)	0.40602(18)	4.30(11)
C(5)	0.6010(3)	0.31422(21)	0.74540(17)	4.03(10)
C(6)	0.4598(3)	0.26898(25)	0.78084(19)	5.22(13)
C(7)	0.4614(4)	0.28603(28)	0.88700(21)	5.90(14)
C(8)	0.5990(4)	0.34895(26)	0.95827(20)	5.56(14)
C(9)	0.7392(3)	0.39415(26)	0.91995(20)	5.58(13)
C(10)	0.7416(3)	0.37713(23)	0.81451(19)	4.77(11)
C(11)	0.5990(5)	0.36928(33)	1.07392(22)	7.75(20)
C(12)	0.4208(3)	0.15802(19)	0.29859(16)	3.63(9)
C(13)	0.3563(3)	0.26849(20)	0.30839(16)	3.93(10)
C(14)	0.2479(3)	0.28715(23)	0.22654(19)	4.51(111)
C(15)	0.2044(3)	0.19567(26)	0.13566(18)	5.02(13)
C(16)	0.2677(3)	0.08536(25)	0.12494(19)	5.27(13)
C(17)	0.3766(3)	0.06640(21)	0.20566(18)	4.59(11)
C(18)	0.8949(3)	0.21879(20)	0.33809(17)	3.91(10)
C(19)	0.9958(3)	0.18987(24)	0.41770(19)	4.87(12)
C(20)	1.0436(3)	0.07175(28)	0.40067(24)	5.68(14)
C(21)	0.9898(3)	-0.01479(25)	0.30667(25)	5.66(15)
C(22)	0.8887(4)	0.01864(25)	0.22925(21)	5.62(13)
C(23)	0.8411(3)	0.13538(23)	0.24384(19)	4.83(12)
C(24)	1.0442(5)	-0.14212(30)	0.28962(32)	8.57(22)
N(1)	0.60401(22)	0.29426(17)	0.63614(13)	3.87(8)
N(2)	0.71176(22)	0.37930(17)	0.59747(14)	4.10(9)
N(3)	0.57549(22)	0.21766(16)	0.47255(13)	3.81(8)
N(4)	0.53790(23)	0.13585(16)	0.37615(14)	4.15(8)
N(5)	0.84954(22)	0.34360(16)	0.35278(14)	3.96(8)
N(6)	0.89627(26)	0.41890(19)	0.28973(16)	5.16(10)
O(1)	0.41248(19)	0.10048(14)	0.56842(12)	4.46(8)
O(2)	0.83890(22)	0.52914(15)	0.32102(13)	5.25(9)
O(3)	0.69237(23)	0.60462(15)	0.44208(14)	5.62(9)
H(6)	0(0)	0(0)	1(0)	6(0)
H(7)	0(0)	0(0)	1(0)	6(0)
H(9)	1(0)	0(0)	1(0)	6(0)
H(10)	1(0)	0(0)	1(0)	5(0)
H(11a)	0(0)	0(0)	1(0)	8(0)
H(11b)	1(0)	0(0)	1(0)	8(0)
H(11c)	1(0)	0(0)	1(0)	8(0)
H(13)	0(0)	0(0)	0(0)	5(0)
H(14)	0(0)	0(0)	0(0)	5(0)
H(16)	0(0)	0(0)	0(0)	6(0)
H(17)	0(0)	0(0)	0(0)	5(0)
H(19)	1(0)	0(0)	0(0)	6(0)
H(20)	1(0)	0(0)	0(0)	6(0)
H(22)	1(0)	0(0)	0(0)	6(0)
H(23)	1(0)	0(0)	0(0)	5(0)
H(24a)	1(0)	0(0)	0(0)	10(0)
H(24b)	1(0)	0(0)	0(0)	10(0)
H(24c)	1(0)	0(0)	0(0)	10(0)
H(N4)	1(0)	0(0)	0(0)	5(0)

N: 19.37. found C: 49.69, H: 6.33, N: 19.37.

4-Methylphenylhydrazine hydrochloride (1b)

White powder; mp 233~233.5 °C, IR (KBr), cm^{-1}: 3214 (νN-H), 3174~2780 [(-NH_3^+)νN-H], ^1H NMR (DMSO-d_6), δ= 10.12 (br, 3H), 7.08 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 7.6 Hz, 2H), 2.21 (s, 3H), EIMS (70eV), *m/z* (%): 122 (M^+-36, 100), 106 (89), 91 (38), 79 (54), 77 (52), 65 (18). Anal.Calcd. for $C_7H_{11}N_2Cl$ (158.63) C: 53.00, H: 6.99, N: 17.66. found C: 53.03, H: 7.11, N: 17.71.

4-Ethoxyphenylhydrazine hydrochloroide (1c)

Pale brown powder; mp 165.5~166.5 °C, IR (KBr), cm^{-1}: 3208 (νN-H) , 3180~2790 [(-NH_3^+)νN-H], ^{1}H NMR (DMSO-d_6), δ= 10.12 (br, 3H), 6.99 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 3.93 (q, J = 7.7 Hz, 2H), 1.27 (t, J = 7.7 Hz, 3H), EIMS (70 eV), *m/z* (%): 152 (M^+-36, 100), 140 (89), 125 (62), 93 (76), 77 (52), 65 (63). Anal. Calcd. for $C_8H_{13}N_2OCl$ (188.66), C: 50.93, H: 6.95, N: 14.85. found C: 50. 88, H: 6.89, N: 14.88.

4-Chlorophenylhydrazine hydrochloride (1d)

White powder; mp 223~224 °C, IR (KBr), cm^{-1}: 3208 (νN-H) , 3175~2780 [(-NH_3^+)νN-H], ^{1}H NMR (DMSO-d_6), δ = 10.43 (br, 3H), 7.30 (d, J = 9.0Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), EIMS (70 eV), *m/z* (%): 144 (M^+-34, 42), 142 (M^+-36, 100), 128 (23), 126 (84), 99 (57), 77 (32), 63 (26). Anal. Calcd. for $C_6H_8N_2Cl_2$ (179.05) C: 40.25, H: 4.50, N: 15.65. found C: 40.18, H: 4.59, N: 15.55.

4-Fluorophenylhydrazine hydrochloride (1e)

White powder, mp 216 °C (dec.), IR(KBr), cm^{-1}: 3208 (νN-H) , 3175~2750 [(-NH_3^+)νN-H], ^{1}H NMR (DMSO-d_6), δ = 10.29 (br, 3H), 7.18~6.90 (m, 4H), EIMS (70 eV), *m/z* (%): 126 (M^+-36, 100), 110 (76), 95 (14), 83 (75). Anal.Calcd. for $C_6H_8N_2FCl$ (162.59) C: 44.33, H: 4.96, N: 17.23. found C: 44.35, H: 4.94, N: 17.31.

4-Ethoxycarbonylphenylhydrazine hydrochloride (1f)

White powder, mp 220~221 °C, IR (KBr), cm^{-1}: 3208 (νN-H) , 3185~2755 [(-NH_3^+)ν N-H], 1713 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 10.58 (br, 3H), 8.99 (br, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), EIMS (70 eV), *m/z* (%): 180 (M^+-36, 100), 152 (23), 135 (95), 107 (12), 90 (12). Anal.Calcd. for $C_9H_{13}N_2O_2Cl$ (214.69) , C: 50.35, H: 6.10, N: 13.05. found C: 50.07, H: 6.04, N: 12.97.

4-Nitrophenylhydrazine hydrochloride (1g)

Yellow powder, mp 201~202 °C, IR (KBr), cm^{-1}: 3320 (νN-H) , 3171~2785 [(-NH_3^+)νN-H], ^{1}H NMR (DMSO-d_6), δ = 10.74 (br, 3H), 9.55 (br, 1H), 8.16 (d, J = 10.3 Hz, 2H), 7.05 (d, J = 10.3 Hz, 2H), EIMS (70 eV), *m/z* (%): 153 (M^+-36, 100), 137 (72), 123(78), 107 (57), 91 (82), 76 (69), 65 (57), 30 (45). Anal. Calcd. for $C_6H_8N_3O_2Cl$ (189.54) C: 38.02, H: 4.25, N: 22.17. found C: 38.04, H: 4.36, N: 22.13.

Syntheses of Semicabazides 3 and Carbazides 4

Typical procedures for the synthesis of **3** and **4** were as follows:

2.37 g (0.01 mol) of α-chloroformyl-4-methoxyphenyl-hydrazine hydrochloride (suspension) in ethyl acetate (50 mL) was added into 4-methoxyaniline (0.01 mol, 1.23 g) and triethylamine (2.8 mL , 0.02 mol) in 15 mL of ethyl acetate. The reaction mixture was stirred at room temperature for 2 hours. The precipitation solid was collected by filtration, and then transferred into water (100 mL). The crude product was collected by filtration. Also, the organic filtrate was removed under reduced pressure. Further purification was accomplished by adding15 mL of iso-propanol and filtration after stirring for ca. 10 min. The solid products were combined and recrystallized with 95% ethanol to obtain 2,4-dimethoxyphenyl-semicarbazide (**3a**, 2.15 g, 75%).

Carbazides **4** were prepared according to the same procedure.

2,4-Dimethoxyphenylsemicarbazide (3a)

Pale brown needles; mp 177.5 -178.5 °C, IR (KBr), cm^{-1}: 3328 , 3214 (νN-H) , 1650 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 9.20 (s, 1H), 7.47 (d, J = 9.1 Hz, 2H), 7.45 (d, J = 9.1 Hz, 2H), 6.90 (d, J = 10.7 Hz, 2H), 6.83 (d, J = 10.7 Hz, 2H), 5.38 (s, 2H), 3.73 (s, 3H), 3.69 (s, 3H), EIMS (70 eV), *m/z* (%): 287 (M^+, 43), 149 (23), 138 (100), 122 (94), 108 (17), 95 (16). Anal. Calcd. for $C_{15}H_{17}N_3O_3$ (287.32) C: 62.71, H: 5.96, N: 14.63. found C: 62.72, H: 5.93, N: 14.58.

4-(4-Methylphenyl)-2-phenylsemicarbazide (3b)

Colorless needles; mp 172-172.5 °C, IR (KBr), cm^{-1}: 3316, 3208 (νN-H) , 1647 (νC=O), ^{1}H NMR (DMSO-d_6), δ = 9.39 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.11~7.03 (m, 3H), 5.50 (s, 2H), 2.23 (s, 3H), EIMS (70 eV), *m/z* (%): 241 (M^+, 38), 133 (11), 108 (100), 91 (44), 77 (36). Anal. Calcd. for $C_{14}H_{15}N_3O$ (241.29) C: 69.71, H: 6.34, N: 17.46. found C: 69.70, H: 6.30, N: 17.42.

2-(4-Methylphenyl)-4-phenylsemicarbazide (3c)

Colorless needles; mp 177-178 °C, IR (KBr), cm^{-1}: 3322 , 3208 (νN-H) , 1653 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 9.43 (s, 1H), 7.58 (d „J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.24 (t, J = 7.9 Hz, 3H), 7.12 (d, J = 8.2 Hz, 2H), 6.95 (t, J = 7.3, 1H), 5.35 (s, 2H), 2.27 (s, 3H) EIMS (70 eV), *m/z* (%): 241 (M^+, 17), 122 (100), 106 (23), 91 (18). Anal. Calcd. for $C_{14}H_{15}N_3O$ (241.29) C: 69.69, H: 6.26, N: 17.41. found C: 69.76, H: 6.34, N: 17.39.

2,4-Bis-(4-chlorophenyl)-semicarbazide (3d)

Colorless needles; mp 192-192.5 °C, IR (KBr), cm^{-1} 3328 , 3214 (νN-H) , 1644 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 9.66 (s, 1H), 7.69 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 9.0 Hz, 2H), 7.30 (d, J = 9.0 Hz, 2H), 5.55 (s, 2H), EIMS (70 eV), *m/z* (%): 297 (M^++2, 20), 295 (M^+, 30), 153 (26), 144 (76), 142 (100), 126 (58), 111 (16), 99 (24), 90 (23). Anal. Calcd. for $C_{13}H_{11}N_3O_3Cl$ (296.16) C: 52.72, H: 3.74, N: 14.19. found C: 52.73, H: 3.73, N: 14.16.

2-(4-chlorophenyl)-4-(4-fluorophenyl)-semicarbazide (3e)

Colorless needles; mp 171-171.5 °C, IR (KBr), cm^{-1}: 3328 , 3214 (νN-H) , 1644 (ν C=O), ^{1}HNMR (DMSO-d_6), δ = 9.57 (s, 1H), 7.67~7.59 (m, 4H), 7.36 (d, J = 8.9 Hz, 2H),

7.13~7.05 (m, 2H), 5.52 (s, 2H), EIMS (70 eV), *m/z* (%): 279 (M^+, 15), 142 (100), 126 (21), 110 (15), 90(6). Anal. Calcd. for $C_{13}H_{11}N_3OFCl$ (279.70) C: 55.83, H: 3.96, N: 15.02. found C: 55.79, H: 4.06, N: 15.03.

4-(3-chlorophenyl)-2-phenylsemicarbazide (3f)

Pale yellow needles; mp 159.5-160 °C, IR (KBr), cm^{-1}: 3328 , 3214 (νN-H) , 1653 (ν C=O), ^1H NMR (DMSO-d_6), δ = 9.69 (s,1H), 7.86 (t, *J* = 2Hz, 1H), 7.63~7.47 (m, 3H), 7.37~7.23 (m, 3H), 7.13~6.97 (m, 2H), 5.54 (s, 1H), EIMS (70 eV), *m/z* (%): 261 (M^+, 12), 153 (5), 108 (100), 91 (20). Anal. Calcd. for $C_{13}H_{12}N_3OCl$ (261.71) C: 59.66, H: 4.62, N: 16.06. found C: 59.71, H: 4.57, N: 16.16.

4-(4-ethoxycarbonylphenyl)-2-(4-methylphenyl)-semicarbazide (3g)

Pale yellow needles; mp 193-193.5 °C, IR (KBr), cm^{-1}: 3328 , 3214 (νN-H), 1710, 1659 (νC=O), ^{1}HNMR (DMSO-d_6), δ = 9.79 (s, 1H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.53 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), EIMS (70 eV), *m/z* (%): 313 (M^+, 11), 146 (23), 122 (100), 106 (16), 91 (13). Anal. Calcd. for $C_{17}H_{19}N_3O_3$ (313.36) C: 65.16, H: 6.11, N: 13.41. found C: 65.24, H: 6.10, N: 13.43.

4-(4-Methylphenyl)-1-phenylcarbazide (4a)

Colorless needles; mp 164-165 °C, IR (KBr), cm^{-1}: 3328, 3238 (νN-H) , 1671 (ν C=O), ^1H NMR (DMSO-d_6), δ = 8.87 (d, *J* = 2.7 Hz, 1H), 7.48 (d, *J* = 2.7 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.15~7.06 (m, 4H), 6.77~6.62 (m, 3H), 5.25 (s, 2H), 2.24 (s, 3H), EIMS (70 eV), *m/z* (%): 256 (M^+, 34), 134 (100), 122 (56), 106 (42), 91 (39), 77 (61), 65 (29). Anal. Calcd. for $C_{14}H_{16}N_4O$ (256.31) C: 65.61, H: 6.29, N: 21.86. found C: 65.63, H: 6.37, N: 21.96.

4-(4-Chlorophenyl)-1-phenylcarbazide (4b)

Colorless needles; mp 182.5~183.5 °C, IR (KBr), cm^{-1}: 3376, 3334 (νN-H) , 1638 (ν C=O), ^1H NMR (DMSO-d_6), δ = 9.04 (d, *J* = 2.7 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.52 (d, J= 2.7 Hz, 1H), 7.33 (d, *J* = 9.1 Hz, 2H), 7.16-6.63 (m, 5H), 5.35 (s, 2H), EIMS (70 eV), *m/z* (%): 276 (M^+, 44), 154 (61), 142 (72), 126 (20), 106 (80), 92 (40), 77 (100), 65 (36). Anal. Calcd. for $C_{13}H_{13}N_4OCl$ (276.73) C: 56.43, H: 4.74, N: 20.25. found C: 56.48, H: 4.67, N: 20.17.

4-(4-Chlorophenyl)-1-(4-methylphenyl)-carbarzide (4c)

Colorless powder; mp 188~189 °C,IR (KBr), cm^{-1}: 3334, 3323 (νN-H) , 1656 (ν C=O), ^{1}HNMR (DMSO-d_6), δ = 8.99 (d, *J* = 2.3 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.31 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 5.34 (s, 2H), 2.17 (s, 3H), EIMS (70 eV), *m/z* (%): 290 (M^+, 36), 154 (25), 142 (46), 120 (100), 106 (62), 91 (75), 77 (61). Anal. Calcd. for $C_{14}H_{15}N_4OCl$ (290.75) C: 57.83, H: 5.20, N: 19.27. found C: 57.80, H: 5.37, N: 19.23.

1-(4-Ethoxyphenyl)-4-phenylcarbazide (4d)

Colorless needles; mp 181.5~182.5 °C, IR (KBr), cm^{-1}: 3352, 3280 (νN-H) , 1644 (ν C=O), ^1H NMR (DMSO-d_6), δ = 8.89 (d, *J* = 3.3 Hz, 1H), 7.61~7.55 (m, 2H), 7.31~7.23 (m, 2H), 7.14 (d, *J* = 3.3 Hz, 1H), 7.05~6.97 (m, 1H), 6.72 (s, 4H), 5.29 (s, 2H), 3.89 (q, *J* = 6.94 Hz, 2H), 1.26 (t, *J* = 6.94 Hz, 3H), EIMS (70 eV), *m/z* (%): 286 (M^+, 47), 150 (82), 136 (30), 121 (38), 108 (100), 77 (39). Anal. Calcd. for $C_{15}H_{18}N_4O_2$ (286.34) C: 62.92, H: 6.34, N: 19.57. found C: 62.88, H: 6.30, N: 19.59.

1-(4-Ethoxyphenyl)-4-(4-methylphenyl)-carbazide (4e)

Colorless needles; mp 174.5~175.5 °C, IR (KBr), cm^{-1}: 3358, 3302 (νN-H), 1644 (ν C=O), ^{1}HNMR (DMSO-d_6), δ = 8.81 (d, *J* = 3.3 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.11 d, *J* = 3.3 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.72 (s, 4H), 5.22 (s, 2H), 3.89 (q, *J* = 6.9 Hz, 2H), 2.23 (s, 3H), 1.26 (t, *J* = 6.9 Hz, 3H), EIMS (70 eV), *m/z* (%): 300 (M^+, 43), 150 (100), 136 (27), 121 (60), 108 (97), 91 (35). Anal. Calcd. for $C_{16}H_{20}N_4O_2$ (300.6) C: 63.99, H: 6.71, N: 18.65. found C: 63.92, H: 6.78, N: 18.70.

1-(4-Chlorophenyl)-4-(4-methylphenyl)-carbazide (4f)

Colorless needles; mp 184~185 °C , IR (KBr), cm^{-1}: 3358, 3298 (νN-H) , 1659 (ν C=O), ^1H NMR (DMSO-d_6), δ = 8.94 (d, *J* = 2.3 Hz, 1H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 8. 5 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 5.24 (s, 2H), 2.24 (s, 3H), EIMS (70 eV), *m/z* (%): 290 (M^+, 19), 134 (100), 122 (36), 106 (20), 91 (36). Anal. Calcd. for $C_{14}H_{15}N_4OCl$ (290.75) C: 57.83, H: 5.20, N: 19.27. found C: 57.80, H: 5.30, N: 19.30.

1-(4-Fluorophenyl)-4-phenylcarbazide (4g)

Colorless needles; mp 181~182 °C, IR (KBr), cm^{-1}: 3436, 3304 (νN-H) , 1671 (ν C=O), ^1H NMR (DMSO-d_6), δ = 8.97 (d, *J* = 2.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.05~6.92 (m, 3H), 6.79~6.72 (m, 2H), 5.29 (s, 2H), EIMS (70 eV), *m/z* (%): 260 (M^+, 35), 120 (100), 108 (62), 95 (24), 83 (27), 77 (57). Anal. Calcd. for $C_{13}H_{13}N_4OF$ (260.26) C: 59.99, H: 5.04, N: 21.53. found C: 60.06, H: 5.04, N: 21.51.

1-(4-Fluorophenyl)-4-(4-methylphenyl)-carbazide (4h)

Colorless needles; mp 182.5~183 °C, IR (KBr), cm^{-1}: 3328, 3238 (νN-H) , 1668 (ν C=O), ^1H NMR (DMSO-d_6), δ = 8.91 (d, *J* = 2.8 Hz, 1H), 7.46~7.43 (m, 3H), 7.10 ~6.90 (m, 4H), 6.80~6.72 (m,2H), 5.24 (s, 2H), 2.24 (s, 3H), EIMS (70 eV), *m/z* (%): 274 (M^+, 55), 134 (100), 133 (100), 122 (75), 110 (43), 91 (64), 83 (34), 77 (58). Anal. Calcd. for $C_{14}H_{15}N_4OF$ (274.29) C: 61.31, H: 5.51, N: 20.43. found C: 61.37, H: 5.47, N: 20.27.

4-(4-Chlorophenyl)-1-(4-fluorophenyl)-carbazide(4i)

Colorless needles; mp 161~162.4 °C, IR (KBr), cm^{-1}:

3406, 3334 (νN-H) , 1641 (ν C=O), ^{1}HNMR (DMSO-d_6), δ = 9.07 (d, J = 2.0 Hz, 1H), 7.62 (d, J = 9.1 Hz, 2H), 7.48 (d, J = 2.0 Hz, 1H), 7.32 (d, J = 9.1 Hz, 2H), 7.00~6.71 (m, 4H), 5.32 (s, 2H), EIMS (70 eV), *m/z* (%): 294 (M^+, 43), 154 (88), 142 (67), 124 (100), 110 (61), 95 (44), 83 (43), 77 (66). Anal. Calcd. for $C_{13}H_{12}N_4OFCl$ (294.71) C: 52.98, H: 4.10, N: 19.01. found C: 53.05, H: 4.03, N: 19.12.

1-(4-Fluorophenyl)-4-(4-methoxyphenyl)-carbazide (4j)

Colorless needles; mp 170~171 °C, IR (KBr), cm^{-1}: 3364, 3268 (νN-H) , 1647 (ν C=O), ^{1}HNMR (DMSO-d_6), δ = 8.83 (d, J = 2.8 Hz, 1H), 7.45~7.41 (m, 3H), 7.01 ~6.72 (m, 6H), 5.22 (s, 2H), 3.71 (s, 3H), EIMS (70 eV), *m/z* (%): 290 (M^+, 12), 149 (100), 137 (17), 122 (31), 110 (23), 95 (24), 83 (20), 77 (29). Anal. Calcd. for $C_{14}H_{15}N_4O_2F$ (290.29) C: 57.93, H: 5.21, N: 19.30. found C: 58.07, H: 5. 28, N: 19.36.

1-(4-Ethoxycarbonyphenyl)-4-(4-methylphenyl)-carbazide (4k)

Colorless needles; mp 199.5~200 °C, IR (KBr), cm^{-1}: 3352, 3274 (νN-H) , 1698, 1647 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 9.08 (d, J = 1.0 Hz, 1H), 8.25 (d, J = 1.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 5.27 (s, 2H), 4.21 (q, J = 7.09 Hz, 2H), 2.24 (s, 3H), 1.26 (t, J = 7.09 Hz, 3H), EIMS (70 eV), *m/z* (%): 328 (M^+, 32), 283 (10), 180 (10), 150 (50), 134 (100), 122 (78), 106 (37), 91 (46). Anal. Calcd. for $C_{17}H_{20}N_4O_3$ (328.37) C: 62.18, H: 6.14, N: 17.06. found C: 62.29, H: 6.22, N: 17.08.

4-(4-Chlorophenyl)-1-(4-ethoxycarbonyphenyl)-carbazide (4l)

Colorless needles; mp 212.5~213 °C, IR (KBr), cm^{-1}: 3370, 3256 (νN-H) , 1677, 1611 (ν C=O), ^{1}H NMR (DMSO-d_6), δ = 9.25 (d, J = 1.2 Hz, 1H), 8.28 (d, J = 1.2 Hz, 1H), 7.73 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 5.36 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), EIMS (70 eV), *m/z* (%): 348 (M^+, 48), 303 (14), 178 (76), 154 (81), 142 (100), 120 (36), 105 (28), 91 (24), 77 (69). Anal. Calcd. for $C_{16}H_{17}N_4O_3Cl$ (348.79) C: 55.10, H: 4.91, N: 16.06. found C: 55.06, H: 5.07, N: 16.19

Syntheses of Semicabazones 9 and Carbazones 10

Typical procedures for the synthesis of **9** and **10** were as follows:

To a solution of semicarbazide **3a** (0.574 g, 2 mmol) and 3-(4 methoxyphenyl)-4-formylsydnone (0.44 g, 2 mmol) in 25 mL of THF, a drop of sulfuric acid (98%) was added as catalytic agent. The reaction mixture was stirred at room temperature for 1.5 hours, then the solvent was removed under reduced pressure. 15 mL of iso-propanol was added, stirred and the pure powdered product **9a** (0.89 g, 91%) was collected by filtration.

Carbazones **10** were prepared according to this procedure.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2,4-dimethoxyphenyl-semicarbazone (9a)

Green powder; mp 208-209 °C, IR (KBr), cm^{-1}: 3340 (νN-H), 1758, 1692 (ν C=O), 1605 (ν C=N); ^{1}H NMR (DMSO-d_6), δ = 7.95 (s, 1H), 7.77 (d, J = 9.0 Hz, 2H), 7.22~7.04 (m, 8H), 6.94 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), EIMS (70 eV), *m/z* (%): 489 (M^+, 4), 445 (10), 340 (31), 309 (35), 282 (29), 149 (100), 134 (77), 122 (84),108 (44), 92 (26). Anal. Calcd. for $C_{25}H_{23}N_5O_6$ (489.49) C: 61.35, H: 4.74, N: 14.31. found C: 61.25, H: 4.63, N: 14.36.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2-phenyl-4-(4-methyl- phenyl)-semicarbazone (9b)

Yellow powder; mp 215.5-216.5 °C, IR (KBr), cm^{-1}: 3334 (νN-H), 1755, 1704 (ν C=O), 1593 (ν C=N); ^{1}H NMR (DMSO-d_6), δ = 8.21 (s, 1H), 7.77 (d, J = 9.0 Hz,2 H), 7.56~7.48 (m, 3H), 7.27~7.11 (m, 8H), 6.74 (s, 1H), 3.77 (s, 3H), 2.27 (s, 3H), EIMS (70 eV), *m/z* (%): 443 (M^+, 9), 310 (100), 280 (27), 252 (71), 133 (39), 92 (44), 77 (37). Anal. Calcd. for $C_{24}H_{21}N_5O_4$ (443.47) C: 65.00, H: 4.77, N: 15.79. found C: 65.01, H: 4.80, N: 15.77.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2-(4-methyl-phenyl)-4-phenylsemicarbazone (9c)

Pale yellow powder; mp 211.5-212.5 °C, IR (KBr), cm^{-1}: 3370 (νN-H), 1755, 1695 (ν C=O), 1605 (ν C=N); ^{1}H NMR (DMSO-d_6), δ = 8.23 (s, 1H), 7.76 (d, J = 10 Hz, 2H), 7.37~7.04 (m,11H), 6.76 (s, 1H), 3.75 (s, 3H), 2.35 (s, 3H), EIMS (70 eV), *m/z* (%): 443 (M^+, 6), 324 (90), 266 (100), 134 (52), 119 (62), 106 (81), 91 (74). Anal. Calcd. for $C_{24}H_{21}N_5O_4$ (443.47) C: 65.00, H: 4.77, N: 15.79. found C: 65.14, H: 4.88, N: 15.77.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2,4-bis-(4-chloro-phenyl)-semicarbazone (9d)

Yellow powder; mp 223-224 °C, IR (KBr), cm^{-1}: 3364 (νN-H), 1755, 1689 (ν C=O), 1593 (ν C=N); ^{1}H NMR (DMSO-d_6), δ = 8.47 (s, 1H), 7.76 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.37~7.29 (m, 6H), 7.20 (d, J = 9.0 Hz, 2H), 6.79 (s, 1H), 3.78 (s, 3H), EIMS (70 eV), *m/z* (%): 497 (M^+, 7), 397 (10), 344 (24), 313 (49), 300 (43), 286 (30), 153 (100), 134 (77), 127 (62), 111 (51), 90 (49). Anal. Calcd. for $C_{23}H_{17}N_5O_4Cl_2$ (498.38) C: 55.43, H: 3.44, N: 14.05. found C: 55.49, H: 3.44, N: 14.09.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 2-(4-chlorophenyl)-4-(4-fluorophenyl)-semicarbazone (9e)

Yellow powder; mp 212.5-213.5 °C, IR (KBr), cm^{-1}: 3376 (νN-H), 1752, 1695 (ν C=O), 1608 (ν C=N); ^{1}H NMR (DMSO-d_6), δ = 8.28 (s,1H), 7.76 (d, J = 9.1 Hz, 2H), 7.62 (d,

J = 8.6 Hz, 2H), 7.35~7.28 (m, 4H), 7.21~7.12 (m, 4H), 6.78 (s, 1H), 3.75 (s, 3H), EIMS (70 eV), *m/z* (%): 481 (M^+, 6), 421 (22), 344 (52), 300 (30), 286 (59), 134 (100), 111 (36), 92 (24). Anal. Calcd. for $C_{23}H_{17}N_5O_4FCl$ (481.87) C: 57.33, H: 3.56, N: 14.53. found C: 57.21, H: 3.69, N: 14.49.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 4-(3-Chlorophenyl)-2-phenylsemicarbazone (9f)

Pale yellow powder; mp 213-214 °C, IR (KBr), cm^{-1}: 3340 (νN-H), 1746, 1704 (ν C=O), 1605 (ν C=N); ^1H NMR (DMSO-d_6), δ = 8.49 (s, 1H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.61~7.48 (m, 4H), 7.40~7.09 (m, 7H), 6.76 (s, 1H), 3.76 (s, 3H), EIMS (70 eV), *m/z* (%): 463 (M^+, 5), 310 (72), 252 (96), 153(100), 134 (63), 92 (88), 77 (46), 65 (39). Anal. Calcd. for $C_{23}H_{18}N_5O_4Cl$ (463.88) C: 59.55, H: 3.91, N: 15.10. found C: 59. 58, H: 3.84, N: 15.03.

3-(4-Methoxyphenyl)-sydnon-4-ylaldehyde 4-(4-ethoxycarbonyl-phenyl)-2-(4-methylphenyl)-semicarbazone (9g)

yellow powder; mp 225-226 °C, IR (KBr), cm^{-1}: 3334 (νN-H), 1748, 1707 (ν C=O), 1605 (ν C=N); ^1H NMR (DMSO-d_6), δ = 8.70 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 9.1 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 9.1 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.78 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.36 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), EIMS (70 eV), *m/z* (%): 515 (M^+, 20), 469 (10), 324 (41), 266 (55), 191 (27), 146 (100), 106 (68), 91 (45). Anal. Calcd. for $C_{27}H_{25}N_5O_6$ (515.53) C: 62. 91, H: 4.89, N: 13.59. found C: 62.84, H: 4.82, N: 13.54.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 2-(4-methylphenyl)-5-phenylcarbazone (10a)

Yellow powder; mp 195-196 °C, IR (KBr), cm^{-1}: 3412, 3340 (νN-H), 1758, 1701 (ν C=O), 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.41~7.00 (m, 2H), 6.94 (d, *J* = 2.1 Hz, 1H), 6.77~6.57 (m, 4H), 2.34 (s, 3H), 2.11 (s, 3H), EIMS (70 eV), *m/z* (%): 442 (M^+, 34), 308 (26), 250 (33), 134 (43), 106 (75), 91 (100), 77 (62), 65 (46). Anal. Calcd. for $C_{24}H_{22}N_6O_3$ (442.48) C: 65.15, H: 5.01, N: 18.99. found C: 65.13, H: 4.84, N: 19.01.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 2-(4-Chlorophenyl)-5-phenylcarbazone (10b)

Yellow powder; mp 188-189 °C, IR (KBr), cm^{-1}: 3412, 3304 (νN-H), 1758, 1704 (νC=O), 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.25~7.13 (m, 4H), 7.07 (d, *J* = 2.0 Hz, 1H), 6.76 (s, 1H), 6.73~6.58 (m, 3H), 2.14 (s, 3H), EIMS (70 eV), *m/z* (%): 462 (M^+, 5), 400 (21), 342 (24), 328 (15), 270 (20), 199 (26), 153 (24), 118 (58), 105 (24), 91 (100), 77 (61), 65 (55). Anal. Calcd. for $C_{23}H_{19}N_6O_3Cl$ (462.90) C: 59.68, H: 4.14, N: 18.16. found C: 59.65, H: 4.22, N: 18.28.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 2-(4-chlorophenyl)-5-(4-methylphenyl)-carbazone (10c)

Yellow powder; mp 181.5~182.5 °C, IR (KBr), cm^{-1}: 3424, 3358 (νN-H) ,1 755, 1707 (ν C=O), 1614 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 1.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 8.3, 2H), 6.75 (s, 1H), 6.52 (d, *J* = 8.3, 2H), 2.19 (s, 3H), 2.16 (s, 3H), EIMS (70 eV), *m/z* (%): 476 (M^+, 5), 328 (12), 300 (11), 270 (15), 106 (100), 91 (76). Anal. Calcd. for $C_{24}H_{21}N_6O_3Cl$ (476.93) C: 60.44, H: 4.44, N: 17.62. found C: 60.50, H: 4.47, N: 17.64.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-ethoxyphenyl)-2-phenylcarbazone (10d)

Yellow powder; mp 194-195 °C, IR (KBr), cm^{-1}: 3334, 3286 (νN-H), 1758, 1710 (νC=O), 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.57~7.13 (m, 8H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.72 (s, 1H), 6.55 (d, *J* = 8.9 Hz, 2H), 3.92 (q, *J* = 7.0 Hz, 2H), 2.15 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), EIMS (70 eV), *m/z* (%): 472 (M^+, 19), 294 (34), 271 (16), 236 (38), 150 (52), 108 (95), 91 (100), 77 (83), 65 (69). Anal. Calcd. for $C_{25}H_{24}N_6O_4$ (472.51) C: 63.55, H: 5.12 ,N: 17.79. found C: 63.48, H: 5.05, N: 17.70.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-ethoxyphenyl)-2-(4-methylphenyl)-carbazone (10e)

Yellow powder; mp 204.5-205.5 °C, IR (KBr), cm^{-1}: 3370, 3298 (νN-H), 1761, 1692 (νC=O), 1599 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.42~7.30(m, 5H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 2.7 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.71 (s, 1H), 6.53 (d, *J* = 8.9 Hz, 2H), 3.92 (q, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 2.14 (s, 3H), 1.28 (t, *J* = 7.0, 3H), EIMS (70 eV), *m/z* (%): 486 (M^+, 12), 308 (19), 258 (17), 250 (17), 150 (43), 106 (87), 91 (100), 77 (47). Anal. Calcd. for $C_{26}H_{26}N_6O_4$ (486.53) C: 64.19, H: 5.39, N: 17.27. found C: 64.14, H: 5.45, N: 17.23.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-chlorophenyl)-2-(4-methylphenyl)-carbazone (10f)

Yellow powder; mp 194.5~195 °C, IR (KBr), cm^{-1}: 3394, 3358 (νN-H), 1758, 1698 (ν C=O), 1599 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.86 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 1.8 Hz, 1H), 6.73 (s, 1H), 6.50 (d, *J* = 8.8 Hz, 2H), 2.34 (s, 3H), 2.14 (s, 3H), EIMS (70 eV), *m/z* (%): 476 (M^+, 5), 308 (49), 277 (13), 250 (85), 106 (100), 91 (95), 77 (39), 65 (34). Anal. Calcd. for $C_{24}H_{21}N_6O_3Cl$ (476.93) C: 60.44, H: 4.44, N: 17.62. found C: 60.54, H: 4.35, N: 17.52.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-fluorophenyl)-2-phenylcarbazone (10g)

Yellow powder; mp 178.5~179.5 °C, IR (KBr), cm^{-1}:

3352, 3310 (νN-H), 1752, 1701 (νC=O), 1614 (νC=N), ^{1}H NMR (DMSO-d_6), δ =7.71 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 2.0 Hz, 1H), 7.58~7.40 (m, 5H), 7.19~7.02 (m, 4H), 6.97 (d, J = 2.0 Hz, 1H), 6.74 (s, 1H), 6.64~6.58 (m, 2H), 2.15 (s, 3H), EIMS (70 eV), *m/z* (%): 446 (M^+, 33), 294 (25), 236 (36), 146 (16), 126 (41), 106 (49), 91 (100), 77 (88), 65 (53). Anal. Calcd. for $C_{23}H_{19}N_6O_2F$ (446.44) C: 61.88, H: 4.29, N: 18.83. found C: 61.83, H: 4.38, N: 18.79.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-fluorophenyl)-2-(4-methylphenyl)-carbazone (10h)

Yellow powder; mp 126.5~127.5 °C, IR (KBr), cm^{-1}: 3532, 3340 (νN-H) , 1749, 1692 (ν C=O), 1599 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.71 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 2.3 Hz, 1H), 7.41 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.05~6.95 (m, 5H), 6.73 (s, 1H), 6.62~6.55 (m, 2H), 2.34 (s, 3H), 2.14 (s, 3H), EIMS (70 eV), *m/z* (%): 460 (M^+, 9), 308 (20), 294 (12), 250 (36), 236 (19), 150 (16), 106 (61), 91 (100), 77 (49), 65 (50). Anal. Calcd. for $C_{24}H_{21}N_6O_3F$ (460.46) C: 62.60, H: 4.60, N: 18.46. found C: 62.61, H: 4.62, N: 18.36.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-fluorophenyl)-2-(4-methoxyphenyl)-carbazone (10i)

Yellow powder; mp 190~191 °C, IR (KBr), cm^{-1}: 3538, 3340 (νN-H), 1749, 1686 (ν C=O), 1602 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.71 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 2.4 Hz, 1H), 7.41 (d, J = 8.3 Hz, 2H), 7.06~6.96 (m, 7H), 6.74 (s, 1H), 6.62~6.54 (m, 2H), 3.78 (s, 3H), 2.14 (s, 3H), EIMS (70 eV), *m/z* (%): 476 (M^+, 13), 324 (9), 300 (7), 275 (15), 190 (16), 149 (100), 122 (76), 107 (45), 91 (87). Anal. Calcd. for $C_{24}H_{21}N_6O_4F$ (476.46) C: 60.50, H: 4.44, N: 17.64. found C: 60.52, H: 4.42, N: 17.72.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-ethoxy-carbony- phenyl)-2-(4-methylphenyl)-carbazone (10j)

Yellow powder; mp 233~233.5 °C, IR (KBr), cm^{-1}: 3370, 3316 (νN-H), 1764, 1710, 1680 (ν C=O), 1608 (νC=N), ^{1}HNMR (DMSO-d_6), δ = 8.38 (d, J = 1.2 Hz, 1H), 7.79 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 1.2 Hz, 1H), 6.74 (s, 1H), 6.63 (d, J = 8.8 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), FABMS, *m/z* (%): 515 (M^+ +1, 86), Anal. Calcd. for $C_{27}H_{26}N_6O_5$ (514.55) C: 63.03, H: 5.09, N: 16.33. found C: 63.07, H: 5.13, N: 16.20.

3-(4-Methylphenyl)-sydnon-4-ylaldehyde 5-(4-ethoxy-carbonyl- phenyl)-2-(4-chlorophenyl)-carbazone (10k)

Yellow powder; mp 192-193 °C, IR (KBr), cm^{-1}: 3370, 3316 (νN-H), 1767, 1716, 1695 (νC=O), 1608 (νC=N), ^{1}H NMR (DMSO-d_6), δ = 8.40 (d, 1.2 Hz, 1H), 7.80 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.12 (d, 1.2 Hz, 1H), 6.77 (s, 1H), 6.64 (d, J = 8.7 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.13 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), FABMS, *m/z* (%): 535 (M^++1, 83), Anal. Calcd. for $C_{26}H_{23}N_6O_5Cl$ (534.96) C: 58.38, H: 4.33, N: 15.71. found C: 58. 51, H: 4.37, N: 15.68.

Syntheses of 4-(5-oxo-1,2,4-triazol-3-yl)-sydnones 11 and 4-(4-arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones 13

Typical procedures for the synthesis of **11** and **13** were as follows:

Solution of ferric perchlorate hydrate (3 mmoles) and of cupric perchlorate hexahydrate (3 mmoles) in 5 mL acetonitrile were prepared as oxidizing agents.

To 1 mmol of the semicarbazones in 20 mL of acetonitrile, a solution of the oxidizing agent (5 mL) was added. The reaction mixture was stirred at 80 °C for a suitable time (Table 6), then the solvent was removed under reduced pressure. The residue was subjected to chromatography (ethyl acetate : n-hexane = 1 : 2). The eluate was removed under reduced pressure and the pure product was obtained.

1,2,4,5-Tetrazin-3-on-6-ylsydnones **13** were prepared according to the above procedure and the results are shown inTable 7.

4-[1,4-Bis-(4-methoxyphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11a)

Yellow powder; mp 161-162 °C, IR (KBr), cm^{-1}: 1767 , 1713 (ν C=O) , 1650 (ν C=N), ^{1}H NMR (DMSO-d_6), δ = 7.67, (d, J = 9.1 Hz, 2H), 7.48 (d, J = 9.1 Hz, 2H), 7.13~6.90 (m, 8H), 3.85 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), EIMS (70 eV), *m/z* (%): 487 (M^+, 42), 429 (100), 280 (10), 121 (11), 92(8). Anal. Calcd. for $C_{25}H_{21}N_5O_6$ (487.48) C: 61.60, H: 4.34, N: 14.31. found C: 61.62, H: 4.37, N: 14.36.

4-[4-(4-methylphenyl)-5-oxo-1-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11b)

Pale yellow needles; mp 164-165 °C, IR (KBr), cm^{-1}: 1776, 1722 (νC=O), 1599 (νC=N), ^{1}H NMR (DMSO-d_6), δ = 7.80, (d, J = 7.6 Hz, 2H), 7.53~7.45 (m, 4H), 7.33~7.02 (m, 7H), 3.85 (s, 3H), 2.34 (s, 3H), EIMS (70 eV), *m/z* (%): 441 (M^+, 31), 383 (100), 264 (12), 91 (10), 77 (17). Anal. Calcd. for $C_{24}H_{19}N_5O_4$ (441.45) C: 65.30, H: 4.34, N: 15.84. found C: 65.21, H: 4.38, N: 15.98.

4-[1,4-Bis-(4-chlorophenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11d)

Pale yellow powder; mp 170-171 °C,IR (KBr), cm^{-1}: 1776, 1716 (νC=O), 1602 (νC=N), ^{1}H NMR (DMSO-d_6), δ = 7.81 (d, J = 6.8 Hz, 2H), 7.59~7.53 (m, 4H), 7.47 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 7.09 (d, = 7.1 Hz, 2H), 3.85 (s,3 H), EIMS (70 eV), *m/z* (%): 495 (M^+, 22), 439 (65), 437

(100), 125 (16), 111 (11), 92 (18), 77 (19). Anal. Calcd. for $C_{23}H_{15}N_5O_4Cl_2$ (496.37) C: 55.66, H: 3.05, N: 14.11. found C: 55.65, H: 3.05, N: 14.07.

4-[1-(4-Chlorophenyl)-4-(4-fluorophenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11e)

Yellow powder; mp 177-178 °C, IR (KBr), cm^{-1}: 1779 , 1731 (ν C=O) , 1602 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.80, d, J= 9.0 Hz, 2H), 7.58~7.51 (m, 4H), 7.26~7.22 (m, 4H), 7.09 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), EIMS (70 eV), *m/z* (%): 479 (M^+, 24), 437 (11), 421 (100), 125 (16), 92 (17). Anal. Calcd. for $C_{23}H_{15}N_5O_4FCl$ (479.85) C: 57.57, H: 3.15, N: 14.60. found C: 57.65, H: 3.18, N: 14.58.

4-[4-(3-Chlorophenyl)-5-oxo-1-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11f)

Yellow powder; mp 171.5-172.5 °C, IR (KBr), cm^{-1}: 1776 , 1713 (ν C=O) , 1599 (ν C=N), ^1H NMR (DMSO-d_6), δ = 7.78, (d, *J* = 7.9 Hz, 2H), 7.53~7.20 (m, 9H), 7.08 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), EIMS (70 eV), *m/z* (%): 461 (M^+, 22), 403 (100), 119 (13), 91 (19), 77 (26). Anal. Calcd. for $C_{23}H_{16}N_5O_4Cl$ (461.87) C: 59.81, H: 3.49, N: 15.16. found C: 59.83, H: 3.48, N: 15.20.

4-[4-(4-Ethoxycarbonylphenyl)-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methoxyphenyl)-sydnone (11g)

Pale yellow powder; mp 169-170 °C, IR (KBr), cm^{-1}: 1776 , 1722 (ν C=O) ,1605 (ν C=N), ^1H NMR (DMSO-d_6) , δ = 7.95 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 9.1 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 2.31 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H), EIMS (70 eV), *m/z* (%): 513 (M^+, 28), 455 (100), 348 (58), 133 (31), 105 (56), 91 (32), 77 (20), 65 (17). Anal. Calcd. for $C_{27}H_{23}N_5O_6$ (513.51) C: 63.15, H: 4.52, N: 13.64. found C: 63.03, H: 4.38, N: 13.69.

3-(4-Methylphenyl)-4-[1-(4-methylphenyl)-5-oxo-4-phenylamino-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-sydnone(13a)

Yellow needles; mp 164.5 ~165.5 °C, IR (KBr), cm^{-1}: 3328 (νN-H), 1765, 1731 (ν C=O), 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.92 (s, 1H), 7.65~7.56 (m, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 9.55 Hz, 2H), 7.15~6.78 (m, 3H), 6.46 (d, *J* = 8.42 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), EIMS (70 eV), *m/z* (%): 440 (M^+, 29), 382 (42), 318 (25), 290 (37), 105 (48), 91 (100). Anal. Calcd. for $C_{24}H_{20}N_6O_3$ (440.47) C: 65.45, H: 4.58, N: 19.08. found C: 65.31, H: 4.64, N: 19.05.

4-[1-(4-Chlorophenyl)-5-oxo-4-phenylamino-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone(13b)

Yellow needles; mp 173 ~174 °C, IR (KBr), cm^{-1}: 3328 (νN-H) , 1775, 1746 (ν C=O) , 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.91 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), EIMS (70 eV), *m/z* (%): 460 (M^+, 8), 402 (35), 310 (25), 256 (19), 184 (23), 125 (41), 106 (53), 91 (100). Anal. Calcd. for $C_{23}H_{17}N_6O_3Cl$ (460.88) C: 59.94, H: 3.72, N: 18.44. found C: 59.78, H: 3.77, N: 18.35.

4-[1-(4-Chlorophenyl)-4-(4-methylphenylamino)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazo-3-yl]-3-(4-methylphenyl)-sydnone (13c)

Yellow powder; mp 169~170 °C, IR (KBr), cm^{-1}: 3256 (νN-H), 1775, 1728 (ν C=O), 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.77 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.60~7.53 (m, 4H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.37 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H), 2.17 (s, 3H), EIMS (70 eV), *m/z* (%): 474 (M^+, 11), 416 (9), 338 (15), 311 (26), 125 (20), 106 (100), 91 (40). Anal. Calcd. for $C_{24}H_{19}N_6O_3Cl$ (474.91) C: 60.70, H: 4.03, N: 17.70. found C: 60.78, H: 4.05, N: 17.62.

4-[4-(4-Ethoxyphenylamino)-1-(4-methylphenyl)-5oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13d)

Yellow powder; mp 174-175 °C, IR (KBr), cm^{-1}: 3274 (νN-H), 1776, 1728 (ν C=O), 1601 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.63 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.42 (d, *J* = 8.4 Hz, 2H), 3.90 (q, *J* = 6.9 Hz, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 1.27 (t, *J* = 6.9 Hz, 3H), EIMS (70 eV), *m/z* (%): 484 (M^+, 4), 426 (6), 410 (28), 349 (40), 320 (38), 291 (100), 106 (24), 91 (72), 77 (12), 65 (26). Anal. Calcd. for $C_{26}H_{24}N_6O_4$ (484.53) C: 64.45, H: 4.99, N: 17.35. found C: 64.41, H: 4.94, N: 17.32.

4-[4-(4-Chlorophenylamino)-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13e)

Yellow needles; mp 215~216 °C, IR (KBr), cm^{-1}: 3238 (νN-H), 1779, 1707 (ν C=O), 1599 (νC=N), ^1H NMR (DMSO-d_6), δ = 9.03 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* =8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H), EIMS (70 eV), *m/z* (%): 474 (M^+, 15), 416 (15), 348 (17), 318 (40), 290 (38), 105 (46), 91 (100). Anal. Calcd. for $C_{24}H_{19}N_6O_3Cl$ (474.91) C: 60.70, H: 4.03, N: 17.70. found C: 60.78, H: 3.98, N: 17.69.

4-[4-(4-Fluorophenylamino)-5-oxo-1-phenyl-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13f)

Yellow needles; mp 188-189 °C, IR (KBr), cm^{-1}: 3244 (νN-H) , 1779, 1707 (ν C=O) , 1602 (ν C=N), ^1H NMR (DMSO-d_6), δ = 8.89 (s, 1H), 7.78~7.25 (m, 9H), 6.94 (t, *J* = 8.9 Hz, 2H), 6.53~6.47 (m, 2H), 2.37 (s, 3H), EIMS (70 eV), *m/z* (%): 444 (M^+, 8), 386 (13), 334 (26), 304 (51), 276 (65), 159 (16), 105 (31), 91 (100), 77 (75). Anal. Calcd. for

$C_{23}H_{17}N_6O_3F$ (444.42) C: 62.16, H: 3.86, N: 18.91. found C: 62.22, H: 3.95, N: 18.87.

4-[4-(4-Fluorophenylamino)-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13g)

Yellow powder; mp 160.5-161.5 °C, IR (KBr), cm^{-1}: 3250 (νN-H) , 1779, 1710 (ν C=O) , 1602 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.88 (s, 1H), 7.62 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 6.94 (t, J = 8.9 Hz, 2H), 6.52~6.45 (m, 2H), 2.37 (s, 3H), 2.30 (s, 3H), EIMS (70 eV), *m/z* (%): 458 (M^+, 19), 400 (25), 348 (23), 318 (56), 290 (48), 105 (54), 91 (100). Anal. Calcd. for $C_{24}H_{19}N_6O_3F$ (458.45) C: 62.88, H: 4.18, N: 18.33. found C: 62.90, H: 4.25, N: 18.25.

4-[4-(4-Fluorophenylamino)-1-(4-methoxyphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13h)

Yellow needles; mp 153-154 °C, IR (KBr), cm^{-1}: 3214 (νN-H), 1770, 1719 (ν C=O) , 1605 (νC=N), ^1H NMR (DMSO-d_6), δ = 8.87 (s,1H), 7.63 (d, J = 9.1 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 9.1 Hz, 2H), 6.94 (t, J = 8.9 Hz, 2H), 6.51~6.45 (m, 2H), 3.76 (s, 3H), 2.37 (s, 3H), EIMS (70 eV), *m/z* (%): 474 (M^+, 37), 443 (13), 416 (24), 364 (48), 334 (100), 306 (54), 121 (87), 107 (45), 91 (42). Anal. Calcd. for $C_{24}H_{19}N_6O_4F$ (474.45) C: 60.76, H: 4.04, N: 17.71. found C: 60.79, H: 4.04, N: 17.66.

4-[4-(4-Ethoxycarbonylphenylamino)-1-(4-methylphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13i)

Yellow powder; mp 104.5~105.5 °C, IR (KBr), cm^{-1}: 3268 (νN-H), 1776, 1716 , 1698 (ν C=O), 1611 (νC=N), ^1H NMR (DMSO-d_6), δ = 9.42 (s,1H), 7.70~7.53 (m, 6H), 7.32 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 6.51 (d, J = 8.7 Hz, 2H), 4.25 (q, J = 7.0 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.28 (t, J = 7.0 Hz, 3H), EIMS (70 eV), *m/z* (%): 512 (M^+, 11), 481 (10), 454 (21), 291 (35), 105 (42), 91 (100), 77 (20), 65 (39). Anal. Calcd. for $C_{27}H_{24}N_6O_5$ (512.53) C: 63.28, H: 4.72, N: 16.40. found C: 63.24, H: 4.73, N: 16.33.

4-[1-(4-Chlorophenyl)-4-(4-ethoxycarbonylphenylamino)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl]-3-(4-methylphenyl)-sydnone (13j)

Pale yellow powder; mp 168.5~169.5 °C, IR (KBr), cm^{-1}: 3292 (νN-H) , 1782, 1725, 1702 (ν C=O) , 1611 (νC=N), ^1H NMR (DMSO-d_6), δ = 9.42 (s, 1H), 7.79 (d, J = 9.1 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.60~7.53 (m, 4H), 7.31 (d, J = 8.1 Hz, 2H), 6.53 (d, J = 8.7 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), EIMS (70 eV), *m/z* (%): 532 (M^+, 19), 474 (33), 310 (34), 165 (26), 120 (69), 91 (100), 77 (20), 65 (54). Anal. Calcd. for $C_{26}H_{21}N_6O_5Cl$ (532.95) C: 58.60, H: 3.97, N: 15.77. found C: 58.65, H: 3.93, N: 15.73.

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Key Words

α-Chloroformylarylhydrazine hydrochloride; Hydrazine; Semicarbazide; Carbazide; Sydnonylaldehyde semicarbazone; Sydnonylaldehyde carbazone; 4-(5-Oxo-1,2,4-triazol-3-yl)-sydnones; 4-(4-Arylamino-5-oxo-1,2,4-triazol-3-yl)-sydnones.

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