Michael Adducts of Vinyl Sulfones – Source for Thiadiazoles, Oxadiazoles and Triazoles

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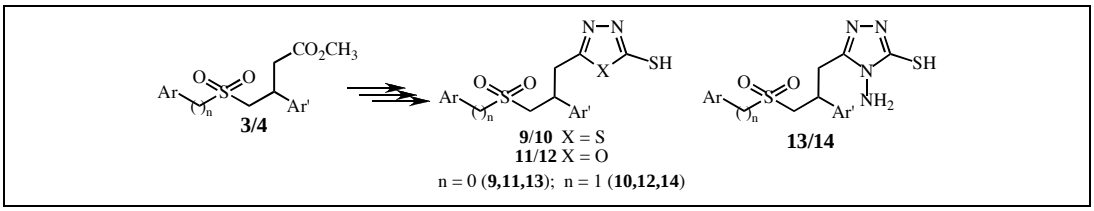
Received March 21, 2008



A new and novel five membered heterocycles thiadiazoles, oxadiazoles and triazoles were prepared from methyl 4-arylsulfonyl-3-arylbutyrate and methyl 4-arylmethanesulfonyl-3-arylbutyrate.

J. Heterocyclic Chem., **45**, 1633 (2008).

INTRODUCTION

Incorporation of heteroatoms in the carbon frame-work to achieve the desired heterocyclic compounds is one of the important aspects in the field of heterocycles. In fact, the chemistry of heterocycles containing nitrogen and sulfur has gained importance due to their varied physiological action and diverse physicochemical properties. The triazole nucleus has a broad spectrum of antimicrobial activity [1]. Bis heterocyclic compounds having both triazole and thiadiazine moieties possess antiparasite activity [2]. The most frequently used triazoles are fluconazole and itraconazole that display a broad spectrum of antifungal activity and reduced toxicity when compared with imidazole antifungals [3-8]. Besides, 2-mercapto-5-methyl-1,3,4-thiadiazole is an intermediate for therapeutically useful antibiotic cefazolin [9]. Moreover, 1,3,4-oxadiazoles find wide usage as dyes, photosensitive and electrical materials [10]. They also exhibit broad spectrum of biological activity such as HIV and antimicrobial [11,12]. In fact, for the last few years we have been involved in the synthesis of a variety of heterocyclic systems. Our continued interest in the field of heterocycles led us to report a new class of five membered heterocycles, thiadiazoles, oxadiazoles and triazoles.

RESULTS AND DISCUSSION

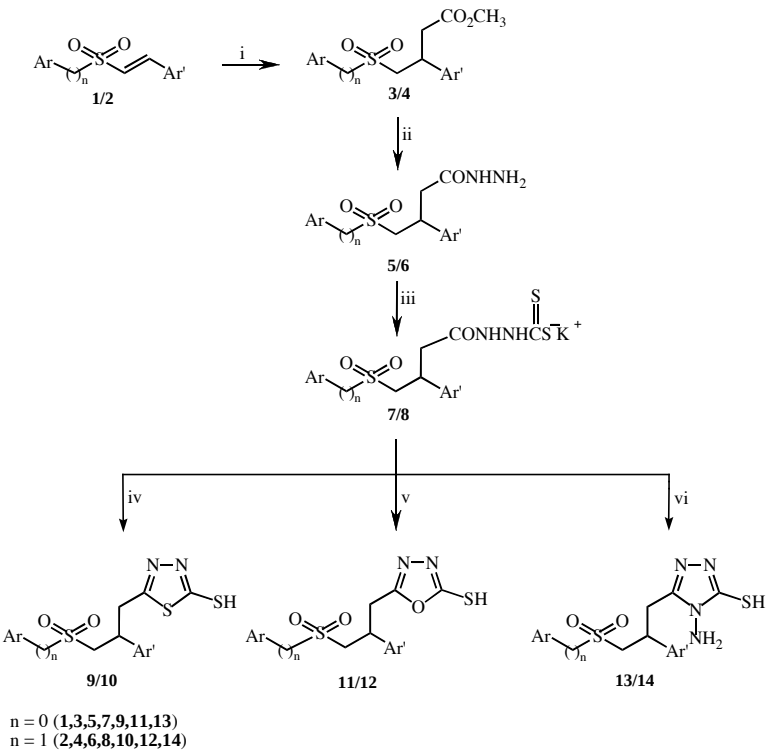
The Michael addition of dimethyl malonate to aryl styryl sulfone (**1**) and benzyl styryl sulfone (**2**) in the presence of Triton-B in toluene gave a product that was identified as methyl 4-arylsulfonyl-3-arylbutyrate (**3**) and methyl 4-arylmethanesulfonyl-3-arylbutyrate (**4**). This shows that during the course of the reaction decarboxylation also took place [13,14]. The IR spectra of **3** and **4** exhibited absorption bands in the regions 1735-1750 for CO_2Me and 1320-1340 and 1120-1150 cm^{-1} for SO_2. The ^1H NMR spectrum of **3a** displayed four double doublets at 2.71, 2.93 (C_2-H), 3.13, 3.22 (C_4-H), a multiplet at 3.79-3.81 (C_3-H) and a singlet at 3.60 (OCH_3) in addition to a multiplet in the region 7.16-7.35 ppm for aromatic protons. The ^1H NMR spectrum of **4a** exhibited signals almost in the same regions as in **3a**. In addition to this, a singlet was observed at 3.93 ppm due to methylene protons flanked between aryl and sulfonyl groups. Treatment of compounds **3** and **4** with hydrazine hydrate gave the corresponding acid hydrazide, 4-arylsulfonyl-3-arylbutanehydrazide (**5**) and 4-arylmethanesulfonyl-3-arylbutanehydrazide (**6**), respectively. The IR spectra of **5** and **6** displayed absorption bands at 1650-1665 for amide carbonyl and at 3325-3335 and 3215-3230 cm^{-1} for NH and NH_2 respectively in addition to the bands due to SO_2. The ^1H NMR spectrum of **5a** displayed four double doublets at 2.68, 2.83 (C_2-H), 3.04, 3.20 (C_4-H) and a multiplet at 3.72-3.76 ppm (C_3-H). Similarly, **6a** also exhibited four double doublets at 2.71, 2.83 (C_2-H), 3.17, 3.23 (C_4-H) and a multiplet at 3.69-3.74 (C_3-H) in addition to a singlet at 4.33 ppm (Ph-CH_2). Apart from these, **5a** and **6a** exhibited broad signals in the regions 7.84-7.94 and 4.44-4.52 ppm for NH and NH_2, which disappeared on deuteration. The potassium dithio-carbazate of the acid hydrazides, **7** and **8** were prepared by treating **5** and **6** with carbon disulfide in the presence potassium hydroxide under ultrasonic conditions. The former compounds under refluxing in acetic acid cyclized to 5-[2'-aryl-3'-(arylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9**) and 5-[2'-aryl-3'-(arylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**10**). On the other hand, acid catalysed hydrolysis of **7** and **8** resulted in 5-[2'-aryl-3'-(arylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11**) and 5-[2'-aryl-3'-(arylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**12**). Besides, 5-[2'-aryl-3'-(arylsulfonyl)propyl]-

1,2,4-triazole-4-amino-3-thiol (**13**) and 5-[2'-aryl-3'-(arylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14**) were obtained by refluxing **7** and **8** with hydrazine hydrate. The IR spectra of the compounds **9**-**14** displayed absorption bands in the regions 1620-1635 for C=N, 2560-2584 cm^{-1} for SH besides bands due to SO_2 group. In addition to these, compounds **13** and **14** exhibited a broad band at 3258-3280 cm^{-1} for NH_2. The ^1H NMR spectra of compounds **9a**-**14a** displayed a singlet in the region 9.78-10.35 ppm for SH. Besides these, two sets of double doublets observed at 2.83, 2.96, 3.08, 3.24 in **9a**, 2.89, 2.97, 3.09, 3.23 in **10a**, 2.86, 3.01, 3.12, 3.23 in **11a**, 2.81, 2.98, 3.14, 3.21 in **12a**, 2.85, 2.97, 3.10, 3.24 in **13a** and 2.82, 2.96, 3.04, 3.17 ppm in **14a** were attributed to C_1'-H and C_3'-H, respectively. A multiplet observed in the region 4.21-4.26 in **9a**, 4.20-4.27 in **10a**, 4.22-4.27 in **11a**, 4.16-4.22 in **12a**, 4.25-4.36 in **13a** and 4.18-4.22 ppm in **14a** was due C_2'-H. Apart from these, compounds **10a**, **12a** and **14a** displayed a singlet at 4.28, 4.32 and 4.26 ppm due to benzylic protons. The compounds **13a** and **14a** showed a broad singlet at 5.49-5.85 ppm for NH_2, which disappeared on deuteration. The structures of the compounds **9**-**14** were further confirmed by ^{13}C NMR spectra.

CONCLUSION

The ester functionality in Michael adducts methyl 4-arylsulfonyl-3-arylbutyrate (**3**) and methyl 4-arylmethanesulfonyl-3-arylbutyrate (**4**) is conveniently utilized to develop thiadiazoles, oxadiazoles and triazoles adopting simple and well-versed methodology.

Scheme 1



	Ar	Ar'
a	Ph	Ph
b	Ph	4-MePh
c	Ph	4-ClPh
d	4-ClPh	Ph
e	4-ClPh	4-ClPh

EXPERIMENTAL

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate/hexane, 1:3). The IR spectra were recorded on a Thermo Nicolet IR200 FT-IR spectrometer as KBr pellets and the wave numbers were given in cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a Varian EM-360 spectrometer (300 MHz). The ^{13}C NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a Varian VXR spectrometer operating at 75.5 MHz. All chemical shifts are reported in δ (ppm) using TMS as an internal standard. The microanalyses were performed on a Perkin-Elmer

240C elemental analyzer. The starting compounds aryl styryl sulfones (**1**) and benzyl styryl sulfones (**2**) were prepared by the literature procedure [14,15].

Methyl 4-arylsulfonyl-3-arylbutyrate (**3**) **and Methyl 4-arylmethanesulfonyl-3-arylbutyrate** (**4**): **General Procedure**. To a solution of aryl styryl sulfone (**1**)/benzyl styryl sulfone (**2**) (1 mmole) and dimethyl malonate (1.5 mmole**s**) in toluene (6 mL) was taken. A catalytic amount of Triton-B was added to the contents of the flask and refluxed for 3-6 hours. The reaction mixture was cooled and the solvent was removed under reduced pressure. The syrupy substance obtained was solidified on treatment with methanol or 2-propanol. The resultant compound was purified by recrystallization from 2-propanol.

Methyl 4-phenylsulfonyl-3-phenylbutyrate (**3a**). This compound was obtained as white solid, mp 109-111°; ir: CO 1747, SO_2 1342, 1139 cm^{-1}; ^1H nmr: δ 2.71 (dd, 1H, C_2-H, *J*=7.9, 15.8 Hz), 2.93 (dd, 1H, C_2-H, *J*=6.1, 16.1 Hz), 3.13 (dd, 1H, C_4-H, *J*=6.7, 13.9 Hz), 3.22 (dd, 1H, C_4-H, *J*=6.4, 14.0 Hz), 3.60 (s, 3H, OCH_3), 3.79-3.81 (m, 1H, C_3-H), 7.16-7.35 (m, 10H, phenyl protons); ^{13}C nmr: δ 35.6 (C-3), 39.7 (C-2), 52.6 (OCH_3), 55.9 (C-4), 172.6 (*C*O_2Me), 125.5, 126.1, 127.8, 129.3, 132.7, 138.5 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.01; H, 5.75.

Methyl 4-phenylsulfonyl-3-(4-methylphenyl)butyrate (**3b**). This compound was obtained as white solid, mp 103-105°; ir: CO 1735, SO_2 1336, 1125 cm^{-1}; ^1H nmr: δ 2.26 (s, 3H, Ar-CH_3), 2.75 (dd, 1H, C_2-H, *J*=7.9, 16.4 Hz), 2.94 (dd, 1H, C_2-H, *J*=5.6, 16.5 Hz), 3.16 (dd, 1H, C_4-H, *J*=7.1, 14.2 Hz), 3.27 (dd, 1H, C_4-H, *J*=7.6, 14.7 Hz), 3.67 (s, 3H, OCH_3), 3.73-3.84 (m, 1H, C_3-H), 7.21-7.82 (m, 9H, phenyl protons); ^{13}C nmr: δ 20.3 (Ar-CH_3), 36.1 (C-3), 38.2 (C-2), 52.9 (OCH_3), 56.3 (C-4), 173.4 (*C*O_2Me), 125.1, 126.8, 128.8, 129.3, 132.1, 138.4 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06. Found: C, 65.11; H, 5.59.

Methyl 4-phenylsulfonyl-3-(4-chlorophenyl)butyrate (**3c**). This compound was obtained as white solid, mp 114-116°; ir: CO 1744, SO_2 1330, 1145 cm^{-1}.

Methyl 4-(4-chlorophenylsulfonyl)-3-phenylbutyrate (**3d**). This compound was obtained as colorless crystals, mp 119-121°; ir: CO 1744, SO_2 1324, 1136 cm^{-1}; ^1H nmr: δ 2.62 (dd, 1H, C_2-H, *J*=7.2, 15.9 Hz), 2.95 (dd, 1H, C_2-H, *J*=6.7, 16.4 Hz), 3.20 (dd, 1H, C_4-H, *J*=6.6, 14.1 Hz), 3.25 (dd, 1H, C_4-H, *J*=7.3, 14.6 Hz), 3.65 (s, 3H, OCH_3), 3.84-3.95 (m, 1H, C_3-H), 7.19-7.45 (m, 9H, phenyl protons); ^{13}C nmr: δ 36.3 (C-3), 41.8 (C-2), 52.9 (OCH_3), 54.8 (C-4), 173.2 (*C*O_2Me), 125.1, 126.4, 127.2, 128.0, 129.9, 130.6, 133.7, 138.4 (aromatic carbons).

Methyl 4-(4-chlorophenylsulfonyl)-3-(4-chlorophenyl)-butyrate (**3e**). This compound was obtained as white solid, mp 112-114°; ir: CO 1741, SO_2 1333, 1142 cm^{-1}; ^1H nmr: δ 2.74 (dd, 1H, C_2-H, *J*=8.1, 16.3 Hz), 2.86 (dd, 1H, C_2-H, *J*=6.4, 16.2 Hz), 3.24 (dd, 1H, C_4-H, *J*=6.8, 14.8 Hz), 3.29 (dd, 1H, C_4-H, *J*=7.5, 14.8 Hz), 3.59 (s, 3H, OCH_3), 3.96-3.98 (m, 1H, C_3-H), 7.21-7.46 (m, 8H, phenyl protons); ^{13}C nmr: δ 36.9 (C-3), 38.6 (C-2), 53.4 (OCH_3), 51.9 (C-4), 173.4 (*C*O_2Me), 126.3, 128.4, 128.9, 129.7, 132.5, 139.8 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{16}Cl_2O_4S$: C, 52.72; H, 4.16. Found: C, 52.65; H, 4.10.

Methyl 4-phenylmethanesulfonyl-3-phenylbutyrate (**4a**). This compound was obtained as white crystals, mp 99-101°; ir: CO 1747, SO_2 1322, 1140 cm^{-1}; ^1H nmr: δ 2.78 (dd, 1H, C_2-H, *J*=8.3, 16.1 Hz), 2.92 (dd, 1H, C_2-H, *J*=6.1, 16.2 Hz), 3.18 (dd, 1H, C_4-H, *J*=6.6, 14.2 Hz), 3.26 (dd, 1H, C_4-H, *J*=6.4, 14.4 Hz), 3.64 (s, 3H, OCH_3), 3.78-3.88 (m, 1H, C_3-H), 3.93 (s, 2H, Ar-CH_2), 7.16-7.49 (m, 10H, phenyl protons); ^{13}C nmr: δ 36.3 (C-3), 40.1 (C-2), 53.2 (OCH_3), 55.1 (C-4), 58.2 (Ar-CH_2), 172.9 (*C*O_2Me), 125.2, 128.8, 129.4, 131.8, 132.9, 138.4 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06. Found: C, 65.15; H, 6.01.

Methyl 4-phenylmethanesulfonyl-3-(4-methylphenyl)-butyrate (**4b**). This compound was obtained as white solid, mp 107-109°; ir: CO 1735, SO_2 1326, 1134 cm^{-1}; ^1H nmr: δ 2.28 (s, 3H, Ar-CH_3), 2.71 (dd, 1H, C_2-H, *J*=7.8, 16.3 Hz), 2.88 (dd, 1H, C_2-H, *J*=6.0, 16.0 Hz), 3.14 (dd, 1H, C_4-H, *J*=6.3, 14.0 Hz), 3.29 (dd, 1H, C_4-H, *J*=6.6, 14.3 Hz), 3.59 (s, 3H, OCH_3), 3.75-3.91 (m, 1H, C_3-H), 3.96 (s, 2H, Ar-CH_2), 7.23-7.56 (m, 9H, phenyl protons); ^{13}C nmr: δ 21.8 (Ar-CH_3), 35.7 (C-3), 40.9 (C-2), 54.6 (OCH_3), 55.9 (C-4), 58.6 (Ar-CH_2), 172.1 (*C*O_2Me), 126.4, 128.0, 129.6, 132.8, 133.2, 139.0 (aromatic carbons).

Methyl 4-phenylmethanesulfonyl-3-(4-chlorophenyl)-butyrate (**4c**). This compound was obtained as colorless needles, mp 118-120°; ir: CO 1744, SO_2 1334, 1131 cm^{-1}; ^1H nmr: δ 2.76 (dd, 1H, C_2-H, *J*=8.1, 16.5 Hz), 2.91 (dd, 1H, C_2-H, *J*=6.2, 16.2 Hz), 3.17 (dd, 1H, C_4-H, *J*=6.1, 14.3 Hz), 3.34 (dd, 1H, C_4-H, *J*=6.8, 14.5 Hz), 3.64 (s, 3H, OCH_3), 3.72-3.89 (m, 1H, C_3-H), 3.94 (s, 2H, Ar-CH_2), 7.19-7.62 (m, 9H, phenyl protons); ^{13}C nmr: δ 35.7 (C-3), 39.4 (C-2), 53.2 (OCH_3), 55.1 (C-4), 57.6 (Ar-CH_2), 172.9 (*C*O_2Me), 125.2, 128.8, 129.9, 131.8, 132.9, 138.4 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{19}ClO_4S$: C, 58.93; H, 5.22. Found: C, 58.89; H, 5.17.

Methyl 4-(4-chlorophenylmethanesulfonyl)-3-phenyl-butyrate (**4d**). This compound was obtained as white solid, mp 121-123°; ir: CO 1741, SO_2 1329, 1141 cm^{-1}.

Methyl 4-(4-chlorophenylmethanesulfonyl)-3-(4-chloro-phenyl)butyrate (**4e**). This compound was obtained as white solid, mp 115-117°; ir: CO 1738, SO_2 1335, 1126 cm^{-1}; ^1H nmr: δ 2.71 (dd, 1H, C_2-H, *J*=8.4, 16.0 Hz), 2.94 (dd, 1H, C_2-H, *J*=6.3, 16.2 Hz), 3.17 (dd, 1H, C_4-H, *J*=6.9, 14.1 Hz), 3.28 (dd, 1H, C_4-H, *J*=6.6, 14.1 Hz), 3.59 (s, 3H, OCH_3), 3.75-3.83 (m, 1H, C_3-H), 3.95 (s, 2H, Ar-CH_2), 7.16-7.35 (m, 8H, phenyl protons); ^{13}C nmr: δ 35.8 (C-3), 39.7 (C-2), 51.8 (OCH_3), 56.2 (C-4), 58.9 (Ar-CH_2), 171.3, (CO_2Me), 125.7, 128.9, 129.2, 131.9, 133.6, 139.2 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{18}Cl_2O_4S$: C, 53.87; H, 4.52. Found: C, 53.82; H, 4.47.

4-Arylsulfonyl-3-arylbutanehydrazide (**5**) **and 4-Aryl-methanesulfonyl-3-arylbutanehydrazide** (**6**): **General Procedure**. To a solution of methyl 4-arylsulfonyl-3-aryl-butyrate (**3**)/methyl 4-arylmethanesulfonyl-3-arylbutyrate (**4**) (1 mmole) in absolute ethanol, hydrazine hydrate (4.5 mmoles) and pyridine (0.4 mL) were added and stirred for 5-6 hours at room temperature. The resultant solid was collected by filtration, dried and recrystallized from ethanol.

4-Phenylsulfonyl-3-phenylbutanehydrazide (**5a**). This compound was obtained as white solid, mp 141-143°; ir: NH 3330, NH_2 3223, CO 1658, SO_2 1330, 1126 cm^{-1}; ^1H nmr: δ 2.68 (dd, 1H, C_2-H, *J*=8.7, 16.7 Hz), 2.83 (dd, 1H, C_2-H, *J*=6.5, 16.2 Hz), 3.04 (dd, 1H, C_4-H, *J*=5.2, 15.0 Hz), 3.20 (dd, 1H, C_4-H, *J*=7.5, 14.8 Hz), 3.72-3.76 (m, 1H, C_3-H), 4.44 (bs, 2H, NH_2), 7.07-7.72 (m, 10H, phenyl protons), 7.84 (bs, 1H, NH); ^{13}C nmr: δ 36.2 (C-3), 39.4 (C-2), 55.7 (C-4), 165.4 (*C*ONH), 124.2, 126.9, 127.7, 128.3, 130.7, 131.4, 135.9, 139.5 (aromatic carbons); *Anal*. Calcd. for $C_{16}H_{18}N_2O_3S$: C, 60.36; H, 5.70; N, 8.80. Found: C, 60.30; H, 5.72; N, 8.84.

4-Phenylsulfonyl-3-(4-methylphenyl)butanehydrazide (**5b**). This compound was obtained as colorless crystals, mp 147-149°; ir: NH 3328, NH_2 3215, CO 1665, SO_2 1320, 1132 cm^{-1}; ^1H

nmr: δ 2.23 (s, 3H, Ar-CH_3), 2.74 (dd, 1H, C_2-H, *J*=8.4, 16.6 Hz), 2.94 (dd, 1H, C_2-H, *J*=6.3, 16.0 Hz), 3.06 (dd, 1H, C_4-H, *J*=6.4, 14.9 Hz), 3.23 (dd, 1H, C_4-H, *J*=7.4, 14.9 Hz), 3.74-3.79 (m, 1H, C_3-H), 4.46 (bs, 2H, NH_2), 7.06-7.53 (m, 9H, phenyl protons), 7.72 (bs, 1H, NH); ^{13}C nmr: δ 21.6 (Ar-CH_3), 36.5 (C-3), 38.9 (C-2), 55.3 (C-4), 166.2 (*C*ONH), 125.8, 126.8, 127.4, 128.3, 130.1, 133.7, 136.6, 139.4 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.45; H, 6.03; N, 8.49.

4-Phenylsulfonyl-3-(4-chlorophenyl)butanehydrazide (**5c**). This compound was obtained as white solid, mp 135-137°; ir: NH 3335, NH_2 3219, CO 1654, SO_2 1335, 1120 cm^{-1}.

4-(4-Chlorophenyl)sulfonyl-3-phenylbutanehydrazide (**5d**). This compound was obtained as white solid, mp 129-131°; ir: NH 3327, NH_2 3224, CO 1660, SO_2 1325, 1141 cm^{-1}; *Anal*. Calcd. for $C_{16}H_{17}ClN_2O_3S$: C, 54.46; H, 4.86; N, 7.94. Found: C, 54.51; H, 4.90; N, 7.85.

4-(4-Chlorophenyl)sulfonyl-3-(4-chlorophenyl)butanehydrazide (**5e**). This compound was obtained as white solid, mp 144-146°; ir: NH 3334, NH_2 3220, CO 1656, SO_2 1334, 1128 cm^{-1}; ^{1}H nmr: δ 2.74 (dd, 1H, C_2-H, *J*=8.1, 16.4 Hz), 2.87 (dd, 1H, C_2-H, *J*=5.7, 15.8 Hz), 3.26 (dd, 1H, C_4-H, *J*=6.8, 14.6 Hz), 3.34 (dd, 1H, C_4-H, *J*=7.0, 14.7 Hz), 3.74-3.82 (m, 1H, C_3-H), 4.58 (bs, 2H, NH_2), 7.15-7.47 (m, 8H, phenyl protons), 7.81 (bs, 1H, NH); ^{13}C nmr: δ 35.9 (C-3), 39.1 (C-2), 55.8 (C-4), 166.5 (*C*ONH), 128.7, 129.4, 131.6, 132.6, 133.8, 134.9, 136.0, 139.4 (aromatic carbons).

4-Phenylmethanesulfonyl-3-phenylbutanehydrazide (**6a**). This compound was obtained as white solid, mp 132-134°; ir NH 3330, NH_2 3218, CO 1662, SO_2 1337, 1134 cm^{-1}; ^{1}H nmr: δ 2.71 (dd, 1H, C_2-H, *J*=8.2, 16.1 Hz), 2.83 (dd, 1H, C_2-H, *J*=6.3, 16.1 Hz), 3.17 (dd, 1H, C_4-H, *J*=6.7, 14.8 Hz), 3.23 (dd, 1H, C_4-H, *J*=7.1, 14.9 Hz), 3.69-3.74 (m, 1H, C_3-H), 4.52 (bs, 2H, NH_2), 4.33 (s, 2H, Ar-CH_2),7.11-7.48 (m, 10H, phenyl protons), 7.94 (bs, 1H, NH); ^{13}C nmr: δ 37.8 (C-3), 40.4 (C-2), 53.8 (C-4), 59.5 (Ar-CH_2), 165.7 (*C*ONH), 126.5, 127.6, 128.9, 129.4, 130.7, 131.3, 139.4 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.34; H, 6.10; N, 8.47.

4-Phenylmethanesulfonyl-3-(4-methylphenyl)butanehydrazide (**6b**). This compound was obtained as white solid, mp 127-129°; ir: NH 3335, NH_2 3212, CO 1655, SO_2 1327, 1123 cm^{-1}; ^{1}H nmr: δ 2.28 (s, 3H, Ar-CH_3), 2.74 (dd, 1H, C_2-H, *J*=8.4, 16.6 Hz), 2.90 (dd, 1H, C_2-H, *J*=6.6, 16.4 Hz), 3.06 (dd, 1H, C_4-H, *J*=7.3, 14.8 Hz), 3.26 (dd, 1H, C_4-H, *J*=9.4, 14.9 Hz), 3.72-3.76 (m, 1H, C_3-H), 4.48 (bs, 2H, NH_2), 4.37 (s, 2H, Ar-CH_2), 7.02-7.35 (m, 9H, phenyl protons), 7.88 (bs, 1H, NH); ^{13}C nmr: δ 20.6 (Ar-CH_3), 37.4 (C-3), 40.7 (C-2), 53.5 (C-4), 58.9 (Ar-CH_2), 166.2 (*C*ONH), 125.8, 128.4, 128.8, 129.8, 131.4, 133.5, 138.7 (aromatic carbons).

4-Phenylmethanesulfonyl-3-(4-chlorophenyl)butanehydrazide (**6c**). This compound was obtained as white solid, mp 142-144°; ir: NH 3331, NH_2 3221, CO 1652, SO_2 1332, 1143 cm^{-1}; *Anal*. Calcd. for $C_{17}H_{19}ClN_2O_3S$: C, 55.66; H, 5.22; N, 7.64. Found: C, 55.70; H, 5.26; N, 7.69.

4-(4-Chlorophenylmethanesulfonyl)-3-phenylbutanehydrazide (**6d**). This compound was obtained as white solid, mp 137-139°; ir: NH 3328, NH_2 3228, CO 1657, SO_2 1337, 1142 cm^{-1}; ^{1}H nmr: δ 2.75 (dd, 1H, C_2-H, *J*=7.5, 16.8 Hz), 2.95 (dd, 1H, C_2-H, *J*=6.3, 16.2 Hz), 3.18 (dd, 1H, C_4-H, *J*=7.0, 15.0 Hz), 3.28 (dd, 1H, C_4-H, *J*=6.7, 14.8 Hz), 3.75-3.82 (m, 1H, C_3-H), 4.57 (bs, 2H, NH_2), 4.36 (s, 2H, Ar-CH_2), 7.08-7.47 (m, 9H, phenyl protons), 7.86 (bs, 1H, NH); ^{13}C nmr: δ 37.6 (C-3), 39.8 (C-2), 54.3 (C-4), 58.7 (Ar-CH_2), 165.5 (*C*ONH), 125.8, 126.7, 128.6, 129.5, 132.4, 137.8, 140.5 (aromatic carbons).

4-(4-Chlorophenylmethanesulfonyl)-3-(4-chlorophenyl)-butanehydrazide (**6e**). This compound was obtained as white solid, mp 147-149°; ir: NH 3326, NH_2 3225, CO 1650, SO_2 1338, 1144 cm^{-1}; *Anal*. Calcd. for $C_{17}H_{18}Cl_2N_2O_3S$: C, 50.88; H, 4.52; N, 6.98. Found: C, 50.94; H, 4.55; N, 6.93.

Potassium (3-aryl-4-arylsulfonyl-1-butanoyl)hydrazine-N'-carbodithioate (**7**) **and Potassium (3-aryl-4-arylmethanesulfonyl-1-butanoyl)hydrazine-N'-carbodithioate** (**8**): **General procedure**. To a mixture of potassium hydroxide (2 mmoles) and 4-arylsulfonyl-3-arylbutanehydrazide (**5**)/4-arylmethanesulfonyl-3-arylbutanehydrazide (**6**) (1 mmole) in absolute ethanol (5 mL), carbon disulfide (4 mmoles) was added and sonicated for 10-12 hours. The separated solid was collected by filtration and dried.

5-[2'-Aryl-3'-(arylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9**) **and 5-[2'-Aryl-3'-(arylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol** (**10**): **General procedure.** A mixture of potassium (3-aryl-4-arylsulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**7**)/ potassium (3-aryl-4-arylmethanesulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**8**) (1 mmole) and acetic acid (4 mL) were refluxed for 18-24 hours. The contents of the flask were cooled and poured into crushed ice. The solid obtained was collected by filtration, dried and recrystallized from 2-propanol.

5-[2'-Phenyl-3'-(phenylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9a**). This compound was obtained as white solid, mp 149-151°; ir: SH 2580, CN 1632, SO_2 1320, 1144 cm^{-1}; ^{1}H nmr: δ 2.83 (dd, 1H, C_1'-H, *J*=7.8, 15.7 Hz), 2.96 (dd, 1H, C_1'-H, *J*=6.5, 16.2 Hz), 3.08 (dd, 1H, C_3'-H, *J*=5.9, 14.5 Hz), 3.24 (dd, 1H, C_3'-H, *J*=6.3, 14.9 Hz), 4.21-4.26 (m, 1H, C_2'-H), 7.09-7.54 (m, 10H, phenyl protons), 10.26 (s, 1H, SH); ^{13}C nmr: δ 38.5 (C-2′), 43.2 (C-1′), 55.7 (C-3′), 166.5 (C-2), 168.3 (C-5), 123.5, 125.2, 126.8, 128.1, 129.7, 132.6, 137.8, 139.4 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{16}N_2O_2S_3$: C, 54.23; H, 4.28; N, 7.44. Found: C, 54.18; H, 4.30; N, 7.49.

5-[2'-(4-Methylphenyl)-3'-(phenylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9b**). This compound was obtained as white solid, mp 157-159°; ir: SH 2584, CN 1636, SO_2 1324, 1147 cm^{-1}.

5-[2'-(4-Chlorophenyl)-3'-(phenylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9c**). This compound was obtained as colorless needles, mp 164-166°; ir: SH 2582, CN 1638, SO_2 1322, 1150 cm^{-1}; ^{1}H nmr: δ 2.87 (dd, 1H, C_1'-H, *J*=7.7, 15.9 Hz), 3.02 (dd, 1H, C_1'-H, *J*=6.3, 16.2 Hz), 3.14 (dd, 1H, C_3'-H, *J*=7.0, 14.0 Hz), 3.31 (dd, 1H, C_3'-H, *J*=6.4, 14.9 Hz), 4.18-4.23 (m, 1H, C_2'-H), 7.02-7.62 (m, 9H, phenyl protons), 10.35 (s, 1H, SH); ^{13}C nmr: δ 39.2 (C-2′), 43.5 (C-1′), 55.8 (C-3′), 166.7 (C-2), 168.0 (C-5), 128.8, 129.3, 129.7, 130.8, 131.1, 132.3, 133.6, 138.2 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{15}ClN_2O_2S_3$: C, 49.68; H, 3.68; N, 6.82. Found: C, 49.71; H, 3.71; N, 6.74.

5-[2'-Phenyl-3'-(4-chlorophenylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9d**). This compound was obtained as white solid, mp 141-143°; ir: SH 2578, CN 1635, SO_2 1335, 1138 cm^{-1}.

5-[2'-(4-Chlorophenyl)-3'-(4-chlorophenylsulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**9e**). This compound was obtained as white solid, mp 158-160°; ir: SH 2570, CN 1628, SO_2 1332, 1125 cm^{-1}; ^{1}H nmr: δ 2.91 (dd, 1H, C_1'-H, *J*=7.6, 15.5 Hz), 3.04 (dd, 1H, C_1'-H, *J*=6.1, 16.7 Hz), 3.12 (dd, 1H, C_3'-H, *J*=6.9, 14.6

Hz), 3.27 (dd, 1H, C_3'-H, *J*=6.7, 14.9 Hz), 4.21-4.27 (m, 1H, C_2'-H), 7.11-7.74 (m, 8H, phenyl protons), 10.31 (s, 1H, SH); ^{13}C nmr: δ 39.6 (C-2′), 43.9 (C-1′), 56.4 (C-3′), 166.8 (C-2), 168.2 (C-5), 128.7, 129.3, 129.9, 130.6, 131.5, 131.8, 134.3, 139.4 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{14}Cl_2N_2O_2S_3$: C, 45.84; H, 3.17; N, 6.29. Found: C, 45.78; H, 3.20; N, 6.24.

5-[2'-Phenyl-3'-(phenylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**10a**). This compound was obtained as white solid, mp 145-147°; ir: SH 2583, CN 1633, SO_2 1331, 1138 cm^{-1}; ^{1}H nmr: δ 2.89 (dd, 1H, C_1'-H, *J*=8.3, 15.8 Hz), 2.97 (dd, 1H, C_1'-H, *J*=6.2, 16.7 Hz), 3.09 (dd, 1H, C_3'-H, *J*=6.6, 14.9 Hz), 3.23 (dd, 1H, C_3'-H, *J*=7.0, 14.1 Hz), 4.20-4.27 (m, 1H, C_2'-H), 4.28 (s, 2H, Ar-CH_2), 7.00-7.78 (m, 10H, phenyl protons), 10.29 (s, 1H, SH); ^{13}C nmr: δ 38.4 (C-2′), 44.2 (C-1′), 54.9 (C-3′), 58.1 (Ar-CH_2), 165.7 (C-2), 168.6 (C-5), 125.7, 126.9, 129.2, 130.4, 131.5, 133.7, 135.4, 139.9 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{18}N_2O_2S_3$: C, 55.36; H, 4.65; N, 7.17. Found: C, 55.30; H, 4.64; N, 7.23.

5-[2'-(4-Methylphenyl)-3'-(phenylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**10b**). This compound was obtained as colorless crystals, mp 139-141°; ir: SH 2561, CN 1626, SO_2 1333, 1141 cm^{-1}; ^{1}H nmr: δ 2.27 (s, 3H, Ar-CH_3), 2.88 (dd, 1H, C_1'-H, *J*=8.0, 16.2 Hz), 2.94 (dd, 1H, C_1'-H, *J*=5.9, 16.5 Hz), 3.07 (dd, 1H, C_3'-H, *J*=6.8, 14.4 Hz), 3.18 (dd, 1H, C_3'-H, *J*=6.5, 14.7 Hz), 4.17-4.23 (m, 1H, C_2'-H), 4.24 (s, 2H, Ar-CH_2), 6.96-7.54 (m, 9H, phenyl protons), 10.22 (s, 1H, SH); ^{13}C nmr: δ 21.2 (Ar-CH_3), 38.1 (C-2′), 44.4 (C-1′), 54.6 (C-3′), 59.6 (Ar-CH_2), 166.3 (C-2), 168.2 (C-5), 124.1, 125.6, 127.3, 129.4, 132.5, 134.5, 135.8, 138.2 (aromatic carbons); *Anal*. Calcd. for $C_{19}H_{20}N_2O_2S_3$: C, 56.41; H, 4.98; N, 6.92. Found: C, 56.38; H, 4.93; N, 6.98.

5-[2'-(4-Chlorophenyl)-3'-(phenylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**10c**). This compound was obtained as white solid, mp 151-153°; ir: SH 2562, CN 1629, SO_2 1337, 1128 cm^{-1}.

5-[2'-Phenyl-3'-(4-chlorophenylmethanesulfonyl)propyl]-1,3,4-thiadiazole-2-thiol (**10d**). This compound was obtained as white solid, mp 148-150°; ir: SH 2564, CN 1632, SO_2 1331, 1145 cm^{-1}; ^{1}H nmr: δ 2.95 (dd, 1H, C_1'-H, *J*=8.4, 16.0 Hz), 3.05 (dd, 1H, C_1'-H, *J*=6.6, 16.5 Hz), 3.11 (dd, 1H, C_3'-H, *J*=6.1, 14.3 Hz), 3.25 (dd, 1H, C_3'-H, *J*=7.2, 14.8 Hz), 4.20-4.25 (m, 1H, C_2'-H), 4.23 (s, 2H, Ar-CH_2), 7.02-7.60 (m, 9H, phenyl protons), 10.29 (s, 1H, SH); ^{13}C nmr: δ 37.6 (C-2′), 44.1 (C-1′), 55.5 (C-3′), 59.2 (Ar-CH_2), 166.5 (C-2), 168.9 (C-5), 124.6, 125.5, 126.9, 127.6, 128.4, 131.7, 136.3, 139.9 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{17}ClN_2O_2S_3$: C, 50.87; H, 4.03; N, 6.59. Found: C, 50.90; H, 4.05; N, 6.63.

5-[2'-(4-Chlorophenyl)-3'-(4-chlorophenylmethanesulfonyl)-propyl]-1,3,4-thiadiazole-2-thiol (**10e**). This compound was obtained as white solid, mp 159-161°; ir: SH 2578, CN 1621, SO_2 1338, 1142 cm^{-1}.

5-[2'-Aryl-3'-(arylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11**) **and 5-[2'-Aryl-3'-(arylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol** (**12**): **General procedure.** Potassium (3-aryl-4-arylsulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**7**)/potassium (3-aryl-4-arylmethanesulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**8**) (1 mmole**)** was dissolved in water (6 mL) and acidified with conc. HCl (1-2 mL). The regenerated solid was collected by filtration, dried and purified by recrystallization from 2-propanol.

5-[2'-Phenyl-3'-(phenylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11a**). This compound was obtained as colorless crystals, mp 184-186°; ir: SH 2562, CN 1625, SO_2 1340, 1130 cm^{-1}; ^{1}H nmr: δ 2.86 (dd, 1H, C_1'-H, *J*=7.5, 16.8 Hz), 3.01 (dd, 1H, C_1'-H, *J*=6.2, 16.5 Hz), 3.12 (dd, 1H, C_3'-H, *J*=6.5, 14.4 Hz), 3.23 (dd, 1H, C_3'-H, *J*=6.7, 14.1 Hz), 4.22-4.27 (m, 1H, C_2'-H), 7.11-7.84 (m, 10H, phenyl protons), 9.89 (s, 1H, SH); ^{13}C nmr: δ 38.8 (C-2′), 44.2 (C-1′), 56.3 (C-3′), 163.3 (C-2), 165.8 (C-5), 124.6, 125.5, 127.1, 128.9, 130.4, 133.3, 137.1, 139.5 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{16}N_2O_3S_2$: C, 56.65; H, 4.47; N, 7.77. Found: C, 56.61; H, 4.45; N, 7.83.

5-[2'-(4-Methylphenyl)-3'-(phenylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11b**). This compound was obtained as white solid, mp 179-181°; ir: SH 2564, CN 1628, SO_2 1338, 1135 cm^{-1}; ^{1}H nmr: δ 2.29 (s, 3H, Ar-CH_3), 2.88 (dd, 1H, C_1'-H, *J*=7.9, 16.3 Hz), 2.93 (dd, 1H, C_1'-H, *J*=6.4, 16.3 Hz), 3.08 (dd, 1H, C_3'-H, *J*=6.8, 15.0 Hz), 3.21 (dd, 1H, C_3'-H, *J*=6.3, 14.8 Hz), 4.22-4.26 (m, 1H, C_2'-H), 7.08-7.93 (m, 9H, phenyl protons), 9.98 (s, 1H, SH); ^{13}C nmr: δ 21.6 (Ar-CH_3), 38.2 (C-2′), 43.6 (C-1′), 55.5 (C-3′), 164.2 (C-2), 166.6 (C-5), 125.9, 126.5, 126.9, 128.6, 129.8, 131.7, 138.3, 139.6 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{18}N_2O_3S_2$: C, 57.73; H, 4.84; N, 7.48. Found: C, 57.77; H, 4.86; N, 7.52.

5-[2'-(4-Chlorophenyl)-3'-(phenylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11c**). This compound was obtained as white solid, mp 168-170°; ir: SH 2572, CN 1632, SO_2 1330, 1132 cm^{-1}.

5-[2'-Phenyl-3'-(4-chlorophenylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11d**). This compound was obtained as white solid, mp 188-190°; ir: SH 2586, CN 1623, SO_2 1336, 1128 cm^{-1}; ^{1}H nmr: δ 2.69 (dd, 1H, C_1'-H, *J*=8.3, 15.8 Hz), 2.88 (dd, 1H, C_1'-H, *J*=5.8, 15.9 Hz), 3.10 (dd, 1H, C_3'-H, *J*=6.6, 14.5 Hz), 3.21 (dd, 1H, C_3'-H, *J*=6.8, 14.4 Hz), 4.21-4.26 (m, 1H, C_2'-H), 7.14-7.84 (m, 9H, phenyl protons), 9.78 (s, 1H, SH); ^{13}C nmr: δ 38.9 (C-2′), 44.1 (C-1′), 55.9 (C-3′), 163.3 (C-2), 165.8 (C-5), 125.2, 126.4, 127.3, 129.5, 131.8, 131.9, 133.5, 140.3 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{15}ClN_2O_3S_2$: C, 51.71; H, 3.83; N, 7.09. Found: C, 51.68; H, 3.79; N, 7.14.

5-[2'-(4-Chlorophenyl)-3'-(4-chlorophenylsulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**11e**). This compound was obtained as white solid, mp 194-196°; ir: SH 2564, CN 1626, SO_2 1335, 1120 cm^{-1}.

5-[2'-Phenyl-3'-(phenylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**12a**)**.** This compound was obtained as white crystals, mp 177-179°; ir: SH 2569, CN 1630, SO_2 1334, 1130 cm^{-1}; ^{1}H nmr: δ 2.81 (dd, 1H, C_1'-H, *J*=8.1, 16.1 Hz), 2.98 (dd, 1H, C_1'-H, *J*=6.4, 16.6 Hz), 3.14 (dd, 1H, C_3'-H, *J*=6.2 14.4 Hz), 3.21 (dd, 1H, C_3'-H, *J*=6.5, 14.7 Hz), 4.16-4.22 (m, 1H, C_2'-H), 4.32 (s, 2H, Ar-CH_2), 6.96-7.44 (m, 10H, phenyl protons), 10.26 (s, 1H, SH); ^{13}C nmr: δ 38.2 (C-2′), 45.4 (C-1′), 56.2 (C-3′), 59.8 (Ar-CH_2), 160.7 (C-2), 168.3 (C-5), 125.7, 126.4, 127.1, 127.8, 128.6, 132.5, 137.3, 138.9 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{18}N_2O_3S_2$: C, 57.73; H, 4.84; N, 7.48. Found: C, 57.70; H, 4.80; N, 7.44.

5-[2'-(4-Methylphenyl)-3'-(phenylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**12b**). This compound was obtained as white solid, mp 183-185°; ir: SH 2560, CN 1623, SO_2 1328, 1146 cm^{-1}.

5-[2'-(4-Chlorophenyl)-3'-(phenylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**12c**). This compound was obtained as white solid, mp 159-161°; ir: SH 2580, CN 1627, SO_2 1328, 1134 cm^{-1}; ^{1}H nmr: δ 2.83 (dd, 1H, C_1'-H, *J*=7.9, 15.8 Hz), 2.96 (dd, 1H, C_1'-H, *J*=6.0, 16.2 Hz), 3.07 (dd, 1H, C_3'-H, *J*=6.5, 14.4 Hz), 3.22 (dd, 1H, C_3'-H, *J*=6.8, 14.6 Hz), 4.18-4.22 (m, 1H,

C_2'-H), 4.27 (s, 2H, Ar-CH_2), 7.12-7.88 (m, 9H, phenyl protons), 10.22 (s, 1H, SH); ^{13}C nmr: δ 39.5 (C-2′), 44.9 (C-1′), 55.8 (C-3′), 57.6 (Ar-CH_2), 161.8 (C-2), 170.1 (C-5), 124.9, 125.6, 126.3, 129.4, 130.1, 132.7, 138.4, 140.5 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{17}ClN_2O_3S_2$: C, 52.87; H, 4.19; N, 6.85. Found: C, 52.91; H, 4.15; N, 6.90.

5-[2'-Phenyl-3'-(4-chlorophenylmethanesulfonyl)propyl]-1,3,4-oxadiazole-2-thiol (**12d**). This compound was obtained as white solid, mp 165-167°; ir: SH 2574, CN 1635, SO_2 1325, 1137 cm^{-1}.

5-[2'-(4-Chlorophenyl)-3'-(4-chlorophenylmethanesulfonyl)-propyl]-1,3,4-oxadiazole-2-thiol (**12e**). This compound was obtained as white solid, mp 189-191°; ir: SH 2560, CN 1624, SO_2 1326, 1128 cm^{-1}; ^{1}H nmr: δ 2.89 (dd, 1H, C_1'-H, *J*=7.5, 15.8 Hz), 2.95 (dd, 1H, C_1'-H, *J*=6.3, 16.1 Hz), 3.06 (dd, 1H, C_3'-H, *J*=6.6, 14.0 Hz), 3.17 (dd, 1H, C_3'-H, *J*=6.9, 14.8 Hz), 4.22-4.29 (m, 1H, C_2'-H), 4.33 (s, 2H, Ar-CH_2), 7.15-7.69 (m, 8H, phenyl protons), 10.31 (s, 1H, SH); ^{13}C nmr: δ 39.4 (C-2′), 45.2 (C-1′), 56.9 (C-3′), 59.1 (Ar-CH_2), 160.1 (C-2), 169.7 (C-5), 125.7, 126.5, 127.1, 128.3, 129.6, 133.5, 138.7, 140.1 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{16}Cl_2N_2O_3S_2$: C, 48.76; H, 3.64; N, 6.32. Found: C, 48.70; H, 3.66; N, 6.28.

5-[2'-Aryl-3'-(arylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13**) **and 5-[2'-Aryl-3'-(arylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol** (**14**): **General procedure.** To a solution of potassium (3-aryl-4-arylsulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**7**)/ potassium (3-aryl-4-arylmethanesulfonyl-1-butanoyl)hydrazine-*N*'-carbodithioate (**8**) (1 mmole) in water (6 mL), hydrazine hydrate (2 mmoles) was added and refluxed for 7-9 hours. The contents of the flask were cooled, diluted with water and acidified with acetic acid (2 mL). The separated solid was collected by filtration, dried and recrystallized from 2-propanol.

5-[2'-Phenyl-3'-(phenylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13a**). This compound was obtained as white solid, mp 201-203°; ir: NH_2 3267, SH 2581, CN 1627, SO_2 1326, 1121 cm^{-1}; ^{1}H nmr: δ 2.85 (dd, 1H, C_1'-H, *J*=8.0, 16.2 Hz), 2.97 (dd, 1H, C_1'-H, *J*=6.1, 15.8 Hz), 3.10 (dd, 1H, C_3'-H, *J*=6.4, 15.0 Hz), 3.24 (dd, 1H, C_3'-H, *J*=6.6, 14.8 Hz), 4.25-4.36 (m, 1H, C_2'-H), 5.58 (bs, 2H, NH_2), 7.05-7.49 (m, 10H, phenyl protons), 10.12 (s, 1H, SH); ^{13}C nmr: δ 38.8 (C-2′), 44.5 (C-1′), 55.1 (C-3′), 144.5 (C-3), 169.8 (C-5), 125.8, 128.4, 129.0, 129.8, 132.3, 133.3, 133.9, 135.1 (aromatic carbons); *Anal*. Calcd. for $C_{17}H_{18}N_4O_2S_2$: C, 54.52; H, 4.84; N, 14.96. Found: C, 54.48; H, 4.87; N, 15.00.

5-[2'-(4-Methylphenyl)-3'-(phenylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13b**). This compound was obtained as white solid, mp 199-201°; ir: NH_2 3258, SH 2573, CN 1628, SO_2 1328, 1134 cm^{-1}; *Anal*. Calcd. for $C_{18}H_{20}N_4O_2S_2$: C, 55.65; H, 5.19; N, 14.42. Found: C, 55.71; H, 5.21; N, 14.47.

5-[2'-(4-Chlorophenyl)-3'-(phenylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13c**). This compound was obtained as white solid, mp 207-209°; ir: NH_2 3262, SH 2567, CN 1631, SO_2 1336, 1125 cm^{-1}; ^{1}H nmr: δ 2.89 (dd, 1H, C_1'-H, *J*=8.4, 16.0 Hz), 2.97 (dd, 1H, C_1'-H, *J*=6.3, 16.4 Hz), 3.07 (dd, 1H, C_3'-H, *J*=5.8, 14.4 Hz), 3.18 (dd, 1H, C_3'-H, *J*=6.5, 14.5 Hz), 4.24-4.28 (m, 1H, C_2'-H), 5.54 (bs, 2H, NH_2), 7.08-7.85 (m, 9H, phenyl protons), 10.08 (s, 1H, SH); ^{13}C nmr: δ 38.7 (C-2′), 43.4 (C-1′), 55.6 (C-3′), 144.8 (C-3), 167.5 (C-5), 125.4, 126.1, 127.3, 128.7, 129.8, 131.7, 134.2, 138.1 (aromatic carbons).

5-[2'-Phenyl-3'-(4-chlorophenylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13d**). This compound was obtained as white solid, mp 222-224°; ir: NH_2 3260, SH 2581, CN 1627, SO_2 1340, 1145 cm^{-1}; *Anal*. Calcd. for $C_{17}H_{17}ClN_4O_2S_2$: C, 49.93; H, 4.19; N, 13.70. Found: C, 49.98; H, 4.17; N, 13.74.

5-[2'-(4-Chlorophenyl)-3'-(4-chlorophenylsulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**13e**). This compound was obtained as white solid, mp 217-219°; ir: NH_2 3265, SH 2580, CN 1625, SO_2 1325, 1141 cm^{-1}; ^{1}H nmr: δ 2.90 (dd, 1H, C_1'-H, *J*=7.7, 16.1 Hz), 2.98 (dd, 1H, C_1'-H, *J*=5.9, 16.4 Hz), 3.13 (dd, 1H, C_3'-H, *J*=6.3, 14.2 Hz), 3.25 (dd, 1H, C_3'-H, *J*=7.3, 14.7 Hz), 4.17-4.22 (m, 1H, C_2'-H), 5.52 (bs, 2H, NH_2), 7.11-7.82 (m, 8H, phenyl protons), 10.11 (s, 1H, SH); ^{13}C nmr: δ 38.5 (C-2′), 44.5 (C-1′), 55.2 (C-3′), 144.7 (C-3), 168.2 (C-5), 125.1, 126.9, 128.1, 129.4, 130.4, 131.8, 137.9, 140.1 (aromatic carbons).

5-[2'-Phenyl-3'-(phenylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14a**). This compound was obtained as white solid, mp 189-191°; ir: NH_2 3275, SH 2563, CN 1630, SO_2 1313, 1125 cm^{-1}; ^{1}H nmr: δ 2.82 (dd, 1H, C_1'-H, *J*=7.9, 15.8 Hz), 2.96 (dd, 1H, C_1'-H, *J*=6.0, 16.2 Hz), 3.04 (dd, 1H, C_3'-H, *J*=6.5, 14.8 Hz), 3.17 (dd, 1H, C_3'-H, *J*=6.8, 14.6 Hz), 4.18-4.22 (m, 1H, C_2'-H), 4.26 (s, 2H, Ar-CH_2), 5.82 (bs, 2H, NH_2), 7.12-7.50 (m, 10H, phenyl protons), 10.23 (s, 1H, SH); ^{13}C nmr: δ 39.8 (C-2′), 44.0 (C-1′), 56.7 (C-3′), 59.8 (Ar-CH_2), 142.3 (C-3), 167.8 (C-5), 125.4, 125.9, 126.5, 127.8, 128.5, 133.4, 137.5, 138.6 (aromatic carbons); *Anal*. Calcd. for $C_{18}H_{20}N_4O_2S_2$: C, 55.65; H, 5.19; N, 14.42. Found: C, 55.60; H, 5.22; N, 14.36.

5-[2'-(4-Methylphenyl)-3'-(phenylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14b**). This compound was obtained as white solid, mp 211-213°; ir: NH_2 3271, SH 2579, CN 1626, SO_2 1324, 1132 cm^{-1}; ^{1}H nmr: δ 2.29 (s, 3H, Ar-CH_3), 2.80 (dd, 1H, C_1'-H, *J*=7.7, 16.1 Hz), 2.94 (dd, 1H, C_1'-H, *J*=6.5, 16.2 Hz), 3.08 (dd, 1H, C_3'-H, *J*=6.2, 14.5 Hz), 3.19 (dd, 1H, C_3'-H, *J*=7.1, 14.5 Hz), 4.20-4.25 (m, 1H, C_2'-H), 4.31 (s, 2H, Ar-CH_2), 5.78 (bs, 2H, NH_2), 7.10-7.61 (m, 9H, phenyl protons), 10.28 (s, 1H, SH); ^{13}C nmr: δ 21.3 (Ar-CH_3), 38.6 (C-2′), 44.5 (C-1′), 55.4 (C-3′), 58.3 (Ar-CH_2), 143.5 (C-3), 167.4 (C-5), 124.6, 125.5, 126.9, 127.6, 128.4, 131.7, 136.3, 139.9 (aromatic carbons).

5-[2'-(4-Chlorophenyl)-3'-(phenylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14c**). This compound was obtained as white solid, mp 204-206°; ir: NH_2 3278, SH 2571, CN 1628, SO_2 1328, 1135 cm^{-1}; *Anal*. Calcd. for $C_{18}H_{19}ClN_4O_2S_2$: C, 51.12; H, 4.53; N, 13.25. Found: C, 51.18; H, 4.55; N, 13.31.

5-[2'-Phenyl-3'-(4-chlorophenylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14d**). This compound was obtained as white solid, mp 209-211°; ir: NH_2 3280, SH 2568, CN 1634, SO_2 1325, 1134 cm^{-1}; ^{1}H nmr: δ 2.84 (dd, 1H, C_1'-H, *J*=7.3, 15.3 Hz), 2.99 (dd, 1H, C_1'-H, *J*=6.3, 16.0 Hz), 3.07 (dd, 1H, C_3'-H, *J*=6.4, 14.5 Hz), 3.21 (dd, 1H, C_3'-H, *J*=6.9, 14.6 Hz), 4.21-4.25 (m, 1H, C_2'-H), 4.31 (s, 2H, Ar-CH_2), 5.77 (bs, 2H, NH_2), 7.15-7.82 (m, 9H, phenyl protons), 10.31 (s, 1H, SH); ^{13}C nmr: δ 39.8 (C-2′), 46.2 (C-1′), 55.8 (C-3′), 59.4 (Ar-CH_2), 140.8 (C-3), 166.9 (C-5), 125.8, 126.8, 127.4, 128.3, 130.1, 133.7, 136.6, 139.4 (aromatic carbons).

5-[2'-(4-chlorophenyl)-3'-(4-chlorophenylmethanesulfonyl)-propyl]-1,2,4-triazole-4-amino-3-thiol (**14e**). This compound was obtained as white solid, mp 197-199°; ir: NH_2 3273, SH 2577, CN 1627, SO_2 1319, 1137 cm^{-1}; *Anal*. Calcd. for $C_{18}H_{18}Cl_2N_4O_2S_2$: C, 47.27; H, 3.97; N, 12.25. Found: C, 47.23; H, 3.94; N, 12.29.

Acknowledgement. The authors are thankful to Department of Science and Technology (DST), New Delhi for financial assistance under major research project.

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