

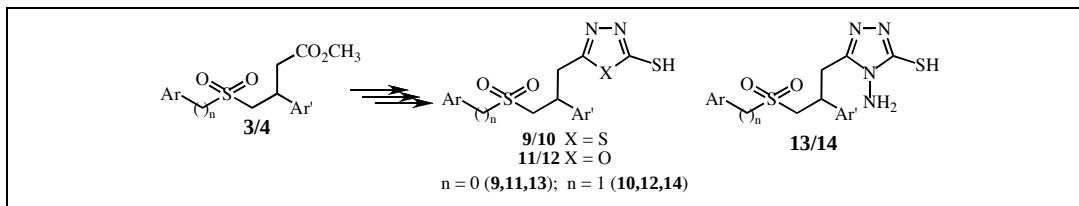
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A new and novel five membered heterocycles thiadiazoles, oxadiazoles and triazoles were prepared from methyl 4-arylsulfonyl-3-arylbutyrate and methyl 4-arylmethanesulfonyl-3-arylbutyrate.

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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 CO₂Me and 1320-1340 and 1120-1150 cm⁻¹ for SO₂. The ¹H NMR spectrum of **3a** displayed four double doublets at 2.71, 2.93 (C₂-H), 3.13, 3.22 (C₄-H), a multiplet at 3.79-3.81 (C₃-H) and a singlet at 3.60 (OCH₃) 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 NH₂ respectively in addition to the bands due to SO₂. The ¹H NMR spectrum of **5a** displayed four double doublets at 2.68, 2.83 (C₂-H), 3.04, 3.20 (C₄-H) and a multiplet at 3.72-3.76 ppm (C₃-H). Similarly, **6a** also exhibited four double doublets at 2.71, 2.83 (C₂-H), 3.17, 3.23 (C₄-H) and a multiplet at 3.69-3.74 (C₃-H) in addition to a singlet at 4.33 ppm (Ph-CH₂). 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 NH₂, which disappeared on deuteration. The potassium dithiocarbamate 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]-

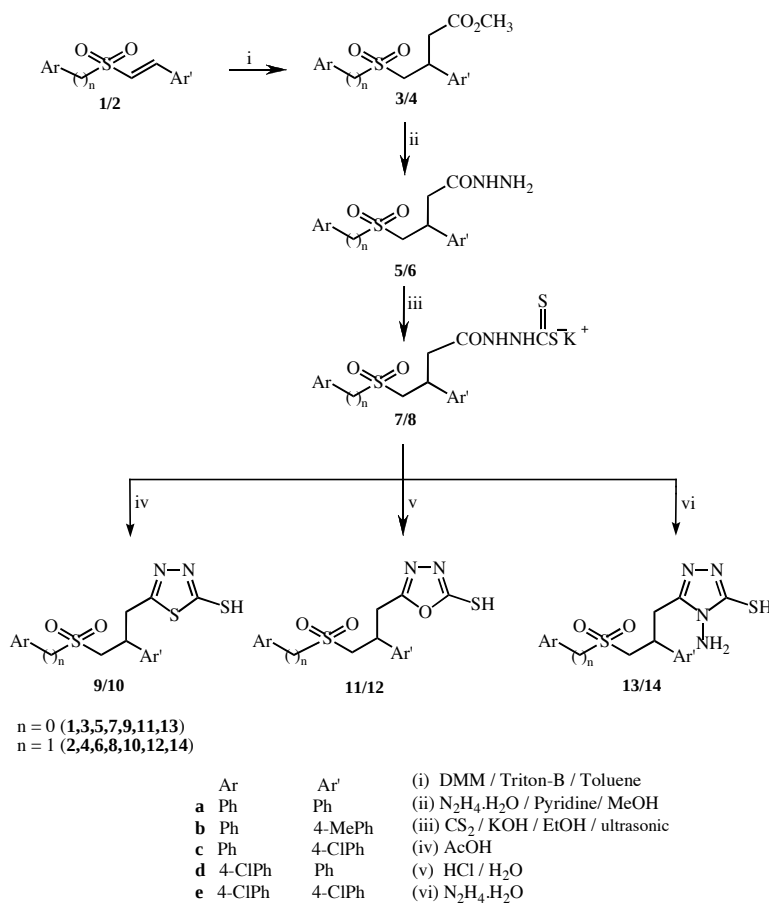
1,2,4-triazole-4-amino-3-thiol (**13**) and 5-[2'-aryl-3'-(arylmethanesulfonyl)propyl]-1,2,4-triazole-4-amino-3-thiol (**14**) were obtained by refluxing **7** and **8** with hydrazine hydrate. The IR spectra of the compounds **9-14** displayed absorption bands in the regions 1620-1635 for C=N, 2560-2584 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

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



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 $\text{C}_1'\text{-H}$ and $\text{C}_3'\text{-H}$, 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 to $\text{C}_2'\text{-H}$. 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

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 $\text{CDCl}_3/\text{DMSO}-d_6$ on a Varian EM-360 spectrometer (300 MHz). The ^{13}C NMR spectra were recorded in $\text{CDCl}_3/\text{DMSO}-d_6$ 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 mmoles) 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, SO₂ 1342, 1139 cm⁻¹; ¹H nmr: δ 2.71 (dd, 1H, C₂-H, J=7.9, 15.8 Hz), 2.93 (dd, 1H, C₂-H, J=6.1, 16.1 Hz), 3.13 (dd, 1H, C₄-H, J=6.7, 13.9 Hz), 3.22 (dd, 1H, C₄-H, J=6.4, 14.0 Hz), 3.60 (s, 3H, OCH₃), 3.79-3.81 (m, 1H, C₃-H), 7.16-7.35 (m, 10H, phenyl protons); ¹³C nmr: δ 35.6 (C-3), 39.7 (C-2), 52.6 (OCH₃), 55.9 (C-4), 172.6 (CO₂Me), 125.5, 126.1, 127.8, 129.3, 132.7, 138.5 (aromatic carbons); *Anal.* Calcd. for C₁₇H₁₈O₄S: 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, SO₂ 1336, 1125 cm⁻¹; ¹H nmr: δ 2.26 (s, 3H, Ar-CH₃), 2.75 (dd, 1H, C₂-H, J=7.9, 16.4 Hz), 2.94 (dd, 1H, C₂-H, J=5.6, 16.5 Hz), 3.16 (dd, 1H, C₄-H, J=7.1, 14.2 Hz), 3.27 (dd, 1H, C₄-H, J=7.6, 14.7 Hz), 3.67 (s, 3H, OCH₃), 3.73-3.84 (m, 1H, C₃-H), 7.21-7.82 (m, 9H, phenyl protons); ¹³C nmr: δ 20.3 (Ar-CH₃), 36.1 (C-3), 38.2 (C-2), 52.9 (OCH₃), 56.3 (C-4), 173.4 (CO₂Me), 125.1, 126.8, 128.8, 129.3, 132.1, 138.4 (aromatic carbons); *Anal.* Calcd. for C₁₈H₂₀O₄S: 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, SO₂ 1330, 1145 cm⁻¹.

Methyl 4-(4-chlorophenylsulfonyl)-3-phenylbutyrate (3d). This compound was obtained as colorless crystals, mp 119-121°; ir: CO 1744, SO₂ 1324, 1136 cm⁻¹; ¹H nmr: δ 2.62 (dd, 1H, C₂-H, J=7.2, 15.9 Hz), 2.95 (dd, 1H, C₂-H, J=6.7, 16.4 Hz), 3.20 (dd, 1H, C₄-H, J=6.6, 14.1 Hz), 3.25 (dd, 1H, C₄-H, J=7.3, 14.6 Hz), 3.65 (s, 3H, OCH₃), 3.84-3.95 (m, 1H, C₃-H), 7.19-7.45 (m, 9H, phenyl protons); ¹³C nmr: δ 36.3 (C-3), 41.8 (C-2), 52.9 (OCH₃), 54.8 (C-4), 173.2 (CO₂Me), 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, SO₂ 1333, 1142 cm⁻¹; ¹H nmr: δ 2.74 (dd, 1H, C₂-H, J=8.1, 16.3 Hz), 2.86 (dd, 1H, C₂-H, J=6.4, 16.2 Hz), 3.24 (dd, 1H, C₄-H, J=6.8, 14.8 Hz), 3.29 (dd, 1H, C₄-H, J=7.5, 14.8 Hz), 3.59 (s, 3H, OCH₃), 3.96-3.98 (m, 1H, C₃-H), 7.21-7.46 (m, 8H, phenyl protons); ¹³C nmr: δ 36.9 (C-3), 38.6 (C-2), 53.4 (OCH₃), 51.9 (C-4), 173.4 (CO₂Me), 126.3, 128.4, 128.9, 129.7, 132.5, 139.8 (aromatic carbons); *Anal.* Calcd. for C₁₇H₁₆Cl₂O₄S: 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, SO₂ 1322, 1140 cm⁻¹; ¹H nmr: δ 2.78 (dd, 1H, C₂-H, J=8.3, 16.1 Hz), 2.92 (dd, 1H, C₂-H, J=6.1, 16.2 Hz), 3.18 (dd, 1H, C₄-H, J=6.6, 14.2 Hz), 3.26 (dd, 1H, C₄-H, J=6.4, 14.4 Hz), 3.64 (s, 3H, OCH₃), 3.78-3.88 (m, 1H, C₃-H), 3.93 (s, 2H, Ar-

CH₂), 7.16-7.49 (m, 10H, phenyl protons); ¹³C nmr: δ 36.3 (C-3), 40.1 (C-2), 53.2 (OCH₃), 55.1 (C-4), 58.2 (Ar-CH₂), 172.9 (CO₂Me), 125.2, 128.8, 129.4, 131.8, 132.9, 138.4 (aromatic carbons); *Anal.* Calcd. for C₁₈H₂₀O₄S: 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, SO₂ 1326, 1134 cm⁻¹; ¹H nmr: δ 2.28 (s, 3H, Ar-CH₃), 2.71 (dd, 1H, C₂-H, J=7.8, 16.3 Hz), 2.88 (dd, 1H, C₂-H, J=6.0, 16.0 Hz), 3.14 (dd, 1H, C₄-H, J=6.3, 14.0 Hz), 3.29 (dd, 1H, C₄-H, J=6.6, 14.3 Hz), 3.59 (s, 3H, OCH₃), 3.75-3.91 (m, 1H, C₃-H), 3.96 (s, 2H, Ar-CH₂), 7.23-7.56 (m, 9H, phenyl protons); ¹³C nmr: δ 21.8 (Ar-CH₃), 35.7 (C-3), 40.9 (C-2), 54.6 (OCH₃), 55.9 (C-4), 58.6 (Ar-CH₂), 172.1 (CO₂Me), 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, SO₂ 1334, 1131 cm⁻¹; ¹H nmr: δ 2.76 (dd, 1H, C₂-H, J=8.1, 16.5 Hz), 2.91 (dd, 1H, C₂-H, J=6.2, 16.2 Hz), 3.17 (dd, 1H, C₄-H, J=6.1, 14.3 Hz), 3.34 (dd, 1H, C₄-H, J=6.8, 14.5 Hz), 3.64 (s, 3H, OCH₃), 3.72-3.89 (m, 1H, C₃-H), 3.94 (s, 2H, Ar-CH₂), 7.19-7.62 (m, 9H, phenyl protons); ¹³C nmr: δ 35.7 (C-3), 39.4 (C-2), 53.2 (OCH₃), 55.1 (C-4), 57.6 (Ar-CH₂), 172.9 (CO₂Me), 125.2, 128.8, 129.9, 131.8, 132.9, 138.4 (aromatic carbons); *Anal.* Calcd. for C₁₈H₁₉ClO₄S: C, 58.93; H, 5.22. Found: C, 58.89; H, 5.17.

Methyl 4-(4-chlorophenylmethanesulfonyl)-3-phenylbutyrate (4d). This compound was obtained as white solid, mp 121-123°; ir: CO 1741, SO₂ 1329, 1141 cm⁻¹.

Methyl 4-(4-chlorophenylmethanesulfonyl)-3-(4-chlorophenyl)butyrate (4e). This compound was obtained as white solid, mp 115-117°; ir: CO 1738, SO₂ 1335, 1126 cm⁻¹; ¹H nmr: δ 2.71 (dd, 1H, C₂-H, J=8.4, 16.0 Hz), 2.94 (dd, 1H, C₂-H, J=6.3, 16.2 Hz), 3.17 (dd, 1H, C₄-H, J=6.9, 14.1 Hz), 3.28 (dd, 1H, C₄-H, J=6.6, 14.1 Hz), 3.59 (s, 3H, OCH₃), 3.75-3.83 (m, 1H, C₃-H), 3.95 (s, 2H, Ar-CH₂), 7.16-7.35 (m, 8H, phenyl protons); ¹³C nmr: δ 35.8 (C-3), 39.7 (C-2), 51.8 (OCH₃), 56.2 (C-4), 58.9 (Ar-CH₂), 171.3, (CO₂Me), 125.7, 128.9, 129.2, 131.9, 133.6, 139.2 (aromatic carbons); *Anal.* Calcd. for C₁₈H₁₈Cl₂O₄S: C, 53.87; H, 4.52. Found: C, 53.82; H, 4.47.

4-Arylsulfonyl-3-arylbutanehydrazide (5) and 4-Arylmethanesulfonyl-3-arylbutanehydrazide (6): General Procedure. To a solution of methyl 4-arylsulfonyl-3-arylbutyrate (**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, NH₂ 3223, CO 1658, SO₂ 1330, 1126 cm⁻¹; ¹H nmr: δ 2.68 (dd, 1H, C₂-H, J=8.7, 16.7 Hz), 2.83 (dd, 1H, C₂-H, J=6.5, 16.2 Hz), 3.04 (dd, 1H, C₄-H, J=5.2, 15.0 Hz), 3.20 (dd, 1H, C₄-H, J=7.5, 14.8 Hz), 3.72-3.76 (m, 1H, C₃-H), 4.44 (bs, 2H, NH₂), 7.07-7.72 (m, 10H, phenyl protons), 7.84 (bs, 1H, NH); ¹³C nmr: δ 36.2 (C-3), 39.4 (C-2), 55.7 (C-4), 165.4 (CONH), 124.2, 126.9, 127.7, 128.3, 130.7, 131.4, 135.9, 139.5 (aromatic carbons); *Anal.* Calcd. for C₁₆H₁₈N₂O₃S: 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, NH₂ 3215, CO 1665, SO₂ 1320, 1132 cm⁻¹; ¹H

nmr: δ 2.23 (s, 3H, Ar-CH₃), 2.74 (dd, 1H, C₂-H, $J=8.4$, 16.6 Hz), 2.94 (dd, 1H, C₂-H, $J=6.3$, 16.0 Hz), 3.06 (dd, 1H, C₄-H, $J=6.4$, 14.9 Hz), 3.23 (dd, 1H, C₄-H, $J=7.4$, 14.9 Hz), 3.74-3.79 (m, 1H, C₃-H), 4.46 (bs, 2H, NH₂), 7.06-7.53 (m, 9H, phenyl protons), 7.72 (bs, 1H, NH); ¹³C nmr: δ 21.6 (Ar-CH₃), 36.5 (C-3), 38.9 (C-2), 55.3 (C-4), 166.2 (CONH), 125.8, 126.8, 127.4, 128.3, 130.1, 133.7, 136.6, 139.4 (aromatic carbons); *Anal.* Calcd. for C₁₇H₂₀N₂O₃S: 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, NH₂ 3219, CO 1654, SO₂ 1335, 1120 cm⁻¹.

4-(4-Chlorophenyl)sulfonyl-3-phenylbutanehydrazide (5d). This compound was obtained as white solid, mp 129-131°; ir: NH 3327, NH₂ 3224, CO 1660, SO₂ 1325, 1141 cm⁻¹; *Anal.* Calcd. for C₁₆H₁₇ClN₂O₃S: 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, NH₂ 3220, CO 1656, SO₂ 1334, 1128 cm⁻¹; ¹H nmr: δ 2.74 (dd, 1H, C₂-H, $J=8.1$, 16.4 Hz), 2.87 (dd, 1H, C₂-H, $J=5.7$, 15.8 Hz), 3.26 (dd, 1H, C₄-H, $J=6.8$, 14.6 Hz), 3.34 (dd, 1H, C₄-H, $J=7.0$, 14.7 Hz), 3.74-3.82 (m, 1H, C₃-H), 4.58 (bs, 2H, NH₂), 7.15-7.47 (m, 8H, phenyl protons), 7.81 (bs, 1H, NH); ¹³C nmr: δ 35.9 (C-3), 39.1 (C-2), 55.8 (C-4), 166.5 (CONH), 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, NH₂ 3218, CO 1662, SO₂ 1337, 1134 cm⁻¹; ¹H nmr: δ 2.71 (dd, 1H, C₂-H, $J=8.2$, 16.1 Hz), 2.83 (dd, 1H, C₂-H, $J=6.3$, 16.1 Hz), 3.17 (dd, 1H, C₄-H, $J=6.7$, 14.8 Hz), 3.23 (dd, 1H, C₄-H, $J=7.1$, 14.9 Hz), 3.69-3.74 (m, 1H, C₃-H), 4.52 (bs, 2H, NH₂), 4.33 (s, 2H, Ar-CH₂), 7.11-7.48 (m, 10H, phenyl protons), 7.94 (bs, 1H, NH); ¹³C nmr: δ 37.8 (C-3), 40.4 (C-2), 53.8 (C-4), 59.5 (Ar-CH₂), 165.7 (CONH), 126.5, 127.6, 128.9, 129.4, 130.7, 131.3, 139.4 (aromatic carbons); *Anal.* Calcd. for C₁₇H₂₀N₂O₃S: 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, NH₂ 3212, CO 1655, SO₂ 1327, 1123 cm⁻¹; ¹H nmr: δ 2.28 (s, 3H, Ar-CH₃), 2.74 (dd, 1H, C₂-H, $J=8.4$, 16.6 Hz), 2.90 (dd, 1H, C₂-H, $J=6.6$, 16.4 Hz), 3.06 (dd, 1H, C₄-H, $J=7.3$, 14.8 Hz), 3.26 (dd, 1H, C₄-H, $J=9.4$, 14.9 Hz), 3.72-3.76 (m, 1H, C₃-H), 4.48 (bs, 2H, NH₂), 4.37 (s, 2H, Ar-CH₂), 7.02-7.35 (m, 9H, phenyl protons), 7.88 (bs, 1H, NH); ¹³C nmr: δ 20.6 (Ar-CH₃), 37.4 (C-3), 40.7 (C-2), 53.5 (C-4), 58.9 (Ar-CH₂), 166.2 (CONH), 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, NH₂ 3221, CO 1652, SO₂ 1332, 1143 cm⁻¹; *Anal.* Calcd. for C₁₇H₁₆ClN₂O₃S: 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, NH₂ 3228, CO 1657, SO₂ 1337, 1142 cm⁻¹; ¹H nmr: δ 2.75 (dd, 1H, C₂-H, $J=7.5$, 16.8 Hz), 2.95 (dd, 1H, C₂-H, $J=6.3$, 16.2 Hz), 3.18 (dd, 1H, C₄-H, $J=7.0$, 15.0 Hz), 3.28 (dd, 1H, C₄-H, $J=6.7$, 14.8 Hz), 3.75-3.82 (m, 1H, C₃-H), 4.57 (bs, 2H, NH₂), 4.36 (s, 2H, Ar-CH₂), 7.08-7.47 (m, 9H,

phenyl protons), 7.86 (bs, 1H, NH); ¹³C nmr: δ 37.6 (C-3), 39.8 (C-2), 54.3 (C-4), 58.7 (Ar-CH₂), 165.5 (CONH), 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, NH₂ 3225, CO 1650, SO₂ 1338, 1144 cm⁻¹; *Anal.* Calcd. for C₁₇H₁₆Cl₂N₂O₃S: 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, SO₂ 1320, 1144 cm⁻¹; ¹H nmr: δ 2.83 (dd, 1H, C₁'-H, $J=7.8$, 15.7 Hz), 2.96 (dd, 1H, C₁'-H, $J=6.5$, 16.2 Hz), 3.08 (dd, 1H, C₃'-H, $J=5.9$, 14.5 Hz), 3.24 (dd, 1H, C₃'-H, $J=6.3$, 14.9 Hz), 4.21-4.26 (m, 1H, C₂'-H), 7.09-7.54 (m, 10H, phenyl protons), 10.26 (s, 1H, SH); ¹³C 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 C₁₇H₁₆N₂O₂S₃: 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, SO₂ 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, SO₂ 1322, 1150 cm⁻¹; ¹H nmr: δ 2.87 (dd, 1H, C₁'-H, $J=7.7$, 15.9 Hz), 3.02 (dd, 1H, C₁'-H, $J=6.3$, 16.2 Hz), 3.14 (dd, 1H, C₃'-H, $J=7.0$, 14.0 Hz), 3.31 (dd, 1H, C₃'-H, $J=6.4$, 14.9 Hz), 4.18-4.23 (m, 1H, C₂'-H), 7.02-7.62 (m, 9H, phenyl protons), 10.35 (s, 1H, SH); ¹³C 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 C₁₇H₁₅ClN₂O₂S₃: 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, SO₂ 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, SO₂ 1332, 1125 cm⁻¹; ¹H nmr: δ 2.91 (dd, 1H, C₁'-H, $J=7.6$, 15.5 Hz), 3.04 (dd, 1H, C₁'-H, $J=6.1$, 16.7 Hz), 3.12 (dd, 1H, C₃'-H, $J=6.9$, 14.6

Hz), 3.27 (dd, 1H, C₃'-H, *J*=6.7, 14.9 Hz), 4.21-4.27 (m, 1H, C₂'-H), 7.11-7.74 (m, 8H, phenyl protons), 10.31 (s, 1H, SH); ¹³C 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 C₁₇H₁₄Cl₂N₂O₂S₃: 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, SO₂ 1331, 1138 cm⁻¹; ¹H nmr: δ 2.89 (dd, 1H, C₁'-H, *J*=8.3, 15.8 Hz), 2.97 (dd, 1H, C₁'-H, *J*=6.2, 16.7 Hz), 3.09 (dd, 1H, C₃'-H, *J*=6.6, 14.9 Hz), 3.23 (dd, 1H, C₃'-H, *J*=7.0, 14.1 Hz), 4.20-4.27 (m, 1H, C₂'-H), 4.28 (s, 2H, Ar-CH₂), 7.00-7.78 (m, 10H, phenyl protons), 10.29 (s, 1H, SH); ¹³C nmr: δ 38.4 (C-2'), 44.2 (C-1'), 54.9 (C-3'), 58.1 (Ar-CH₂), 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 C₁₈H₁₈N₂O₂S₃: 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, SO₂ 1333, 1141 cm⁻¹; ¹H nmr: δ 2.27 (s, 3H, Ar-CH₃), 2.88 (dd, 1H, C₁'-H, *J*=8.0, 16.2 Hz), 2.94 (dd, 1H, C₁'-H, *J*=5.9, 16.5 Hz), 3.07 (dd, 1H, C₃'-H, *J*=6.8, 14.4 Hz), 3.18 (dd, 1H, C₃'-H, *J*=6.5, 14.7 Hz), 4.17-4.23 (m, 1H, C₂'-H), 4.24 (s, 2H, Ar-CH₂), 6.96-7.54 (m, 9H, phenyl protons), 10.22 (s, 1H, SH); ¹³C nmr: δ 21.2 (Ar-CH₃), 38.1 (C-2'), 44.4 (C-1'), 54.6 (C-3'), 59.6 (Ar-CH₂), 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 C₁₉H₂₀N₂O₂S₃: 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, SO₂ 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, SO₂ 1331, 1145 cm⁻¹; ¹H nmr: δ 2.95 (dd, 1H, C₁'-H, *J*=8.4, 16.0 Hz), 3.05 (dd, 1H, C₁'-H, *J*=6.6, 16.5 Hz), 3.11 (dd, 1H, C₃'-H, *J*=6.1, 14.3 Hz), 3.25 (dd, 1H, C₃'-H, *J*=7.2, 14.8 Hz), 4.20-4.25 (m, 1H, C₂'-H), 4.23 (s, 2H, Ar-CH₂), 7.02-7.60 (m, 9H, phenyl protons), 10.29 (s, 1H, SH); ¹³C nmr: δ 37.6 (C-2'), 44.1 (C-1'), 55.5 (C-3'), 59.2 (Ar-CH₂), 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 C₁₈H₁₇ClN₂O₂S₃: 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, SO₂ 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, SO₂ 1340, 1130 cm⁻¹; ¹H nmr: δ 2.86 (dd, 1H, C₁'-H, *J*=7.5, 16.8 Hz), 3.01 (dd, 1H, C₁'-H, *J*=6.2, 16.5 Hz), 3.12 (dd, 1H, C₃'-H, *J*=6.5, 14.4 Hz), 3.23 (dd, 1H, C₃'-H, *J*=6.7, 14.1 Hz), 4.22-4.27 (m, 1H, C₂'-H), 7.11-7.84 (m, 10H, phenyl protons), 9.89 (s, 1H, SH); ¹³C 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 C₁₇H₁₆N₂O₃S₂: 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, SO₂ 1338, 1135 cm⁻¹; ¹H nmr: δ 2.29 (s, 3H, Ar-CH₃), 2.88 (dd, 1H, C₁'-H, *J*=7.9, 16.3 Hz), 2.93 (dd, 1H, C₁'-H, *J*=6.4, 16.3 Hz), 3.08 (dd, 1H, C₃'-H, *J*=6.8, 15.0 Hz), 3.21 (dd, 1H, C₃'-H, *J*=6.3, 14.8 Hz), 4.22-4.26 (m, 1H, C₂'-H), 7.08-7.93 (m, 9H, phenyl protons), 9.98 (s, 1H, SH); ¹³C nmr: δ 21.6 (Ar-CH₃), 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 C₁₈H₁₈N₂O₃S₂: 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, SO₂ 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, SO₂ 1336, 1128 cm⁻¹; ¹H nmr: δ 2.69 (dd, 1H, C₁'-H, *J*=8.3, 15.8 Hz), 2.88 (dd, 1H, C₁'-H, *J*=5.8, 15.9 Hz), 3.10 (dd, 1H, C₃'-H, *J*=6.6, 14.5 Hz), 3.21 (dd, 1H, C₃'-H, *J*=6.8, 14.4 Hz), 4.21-4.26 (m, 1H, C₂'-H), 7.14-7.84 (m, 9H, phenyl protons), 9.78 (s, 1H, SH); ¹³C 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 C₁₇H₁₅ClN₂O₃S₂: 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, SO₂ 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, SO₂ 1334, 1130 cm⁻¹; ¹H nmr: δ 2.81 (dd, 1H, C₁'-H, *J*=8.1, 16.1 Hz), 2.98 (dd, 1H, C₁'-H, *J*=6.4, 16.6 Hz), 3.14 (dd, 1H, C₃'-H, *J*=6.2, 14.4 Hz), 3.21 (dd, 1H, C₃'-H, *J*=6.5, 14.7 Hz), 4.16-4.22 (m, 1H, C₂'-H), 4.32 (s, 2H, Ar-CH₂), 6.96-7.44 (m, 10H, phenyl protons), 10.26 (s, 1H, SH); ¹³C nmr: δ 38.2 (C-2'), 45.4 (C-1'), 56.2 (C-3'), 59.8 (Ar-CH₂), 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 C₁₈H₁₈N₂O₃S₂: 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, SO₂ 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, SO₂ 1328, 1134 cm⁻¹; ¹H nmr: δ 2.83 (dd, 1H, C₁'-H, *J*=7.9, 15.8 Hz), 2.96 (dd, 1H, C₁'-H, *J*=6.0, 16.2 Hz), 3.07 (dd, 1H, C₃'-H, *J*=6.5, 14.4 Hz), 3.22 (dd, 1H, C₃'-H, *J*=6.8, 14.6 Hz), 4.18-4.22 (m, 1H,

C₂'-H), 4.27 (s, 2H, Ar-CH₂), 7.12-7.88 (m, 9H, phenyl protons), 10.22 (s, 1H, SH); ¹³C nmr: δ 39.5 (C-2'), 44.9 (C-1'), 55.8 (C-3'), 57.6 (Ar-CH₂), 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 C₁₈H₁₇ClN₂O₃S₂: 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, SO₂ 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, SO₂ 1326, 1128 cm⁻¹; ¹H nmr: δ 2.89 (dd, 1H, C₁'-H, *J*=7.5, 15.8 Hz), 2.95 (dd, 1H, C₁'-H, *J*=6.3, 16.1 Hz), 3.06 (dd, 1H, C₃'-H, *J*=6.6, 14.0 Hz), 3.17 (dd, 1H, C₃'-H, *J*=6.9, 14.8 Hz), 4.22-4.29 (m, 1H, C₂'-H), 4.33 (s, 2H, Ar-CH₂), 7.15-7.69 (m, 8H, phenyl protons), 10.31 (s, 1H, SH); ¹³C nmr: δ 39.4 (C-2'), 45.2 (C-1'), 56.9 (C-3'), 59.1 (Ar-CH₂), 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 C₁₈H₁₆Cl₂N₂O₃S₂: 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 mmole) 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: NH₂ 3267, SH 2581, CN 1627, SO₂ 1326, 1121 cm⁻¹; ¹H nmr: δ 2.85 (dd, 1H, C₁'-H, *J*=8.0, 16.2 Hz), 2.97 (dd, 1H, C₁'-H, *J*=6.1, 15.8 Hz), 3.10 (dd, 1H, C₃'-H, *J*=6.4, 15.0 Hz), 3.24 (dd, 1H, C₃'-H, *J*=6.6, 14.8 Hz), 4.25-4.36 (m, 1H, C₂'-H), 5.58 (bs, 2H, NH₂), 7.05-7.49 (m, 10H, phenyl protons), 10.12 (s, 1H, SH); ¹³C 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 C₁₇H₁₈N₄O₂S₂: 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: NH₂ 3258, SH 2573, CN 1628, SO₂ 1328, 1134 cm⁻¹; *Anal.* Calcd. for C₁₈H₂₀N₄O₂S₂: 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: NH₂ 3262, SH 2567, CN 1631, SO₂ 1336, 1125 cm⁻¹; ¹H nmr: δ 2.89 (dd, 1H, C₁'-H, *J*=8.4, 16.0 Hz), 2.97 (dd, 1H, C₁'-H, *J*=6.3, 16.4 Hz), 3.07 (dd, 1H, C₃'-H, *J*=5.8, 14.4 Hz), 3.18 (dd, 1H, C₃'-H, *J*=6.5, 14.5 Hz), 4.24-4.28 (m, 1H, C₂'-H), 5.54 (bs, 2H, NH₂), 7.08-7.85 (m, 9H, phenyl protons), 10.08 (s, 1H, SH); ¹³C 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: NH₂ 3260, SH 2581, CN 1627, SO₂ 1340, 1145 cm⁻¹; *Anal.* Calcd. for C₁₇H₁₇ClN₄O₂S₂: 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: NH₂ 3265, SH 2580, CN 1625, SO₂ 1325, 1141 cm⁻¹; ¹H nmr: δ 2.90 (dd, 1H, C₁'-H, *J*=7.7, 16.1 Hz), 2.98 (dd, 1H, C₁'-H, *J*=5.9, 16.4 Hz), 3.13 (dd, 1H, C₃'-H, *J*=6.3, 14.2 Hz), 3.25 (dd, 1H, C₃'-H, *J*=7.3, 14.7 Hz), 4.17-4.22 (m, 1H, C₂'-H), 5.52 (bs, 2H, NH₂), 7.11-7.82 (m, 8H, phenyl protons), 10.11 (s, 1H, SH); ¹³C 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: NH₂ 3275, SH 2563, CN 1630, SO₂ 1313, 1125 cm⁻¹; ¹H nmr: δ 2.82 (dd, 1H, C₁'-H, *J*=7.9, 15.8 Hz), 2.96 (dd, 1H, C₁'-H, *J*=6.0, 16.2 Hz), 3.04 (dd, 1H, C₃'-H, *J*=6.5, 14.8 Hz), 3.17 (dd, 1H, C₃'-H, *J*=6.8, 14.6 Hz), 4.18-4.22 (m, 1H, C₂'-H), 4.26 (s, 2H, Ar-CH₂), 5.82 (bs, 2H, NH₂), 7.12-7.50 (m, 10H, phenyl protons), 10.23 (s, 1H, SH); ¹³C nmr: δ 39.8 (C-2'), 44.0 (C-1'), 56.7 (C-3'), 59.8 (Ar-CH₂), 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 C₁₈H₂₀N₄O₂S₂: 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: NH₂ 3271, SH 2579, CN 1626, SO₂ 1324, 1132 cm⁻¹; ¹H nmr: δ 2.29 (s, 3H, Ar-CH₃), 2.80 (dd, 1H, C₁'-H, *J*=7.7, 16.1 Hz), 2.94 (dd, 1H, C₁'-H, *J*=6.5, 16.2 Hz), 3.08 (dd, 1H, C₃'-H, *J*=6.2, 14.5 Hz), 3.19 (dd, 1H, C₃'-H, *J*=7.1, 14.5 Hz), 4.20-4.25 (m, 1H, C₂'-H), 4.31 (s, 2H, Ar-CH₂), 5.78 (bs, 2H, NH₂), 7.10-7.61 (m, 9H, phenyl protons), 10.28 (s, 1H, SH); ¹³C nmr: δ 21.3 (Ar-CH₃), 38.6 (C-2'), 44.5 (C-1'), 55.4 (C-3'), 58.3 (Ar-CH₂), 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: NH₂ 3278, SH 2571, CN 1628, SO₂ 1328, 1135 cm⁻¹; *Anal.* Calcd. for C₁₈H₁₉ClN₄O₂S₂: 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: NH₂ 3280, SH 2568, CN 1634, SO₂ 1325, 1134 cm⁻¹; ¹H nmr: δ 2.84 (dd, 1H, C₁'-H, *J*=7.3, 15.3 Hz), 2.99 (dd, 1H, C₁'-H, *J*=6.3, 16.0 Hz), 3.07 (dd, 1H, C₃'-H, *J*=6.4, 14.5 Hz), 3.21 (dd, 1H, C₃'-H, *J*=6.9, 14.6 Hz), 4.21-4.25 (m, 1H, C₂'-H), 4.31 (s, 2H, Ar-CH₂), 5.77 (bs, 2H, NH₂), 7.15-7.82 (m, 9H, phenyl protons), 10.31 (s, 1H, SH); ¹³C nmr: δ 39.8 (C-2'), 46.2 (C-1'), 55.8 (C-3'), 59.4 (Ar-CH₂), 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: NH₂ 3273, SH 2577, CN 1627, SO₂ 1319, 1137 cm⁻¹; *Anal.* Calcd. for C₁₈H₁₈Cl₂N₄O₂S₂: C, 47.27; H, 3.97; N, 12.25. Found: C, 47.23; H, 3.94; N, 12.29.

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