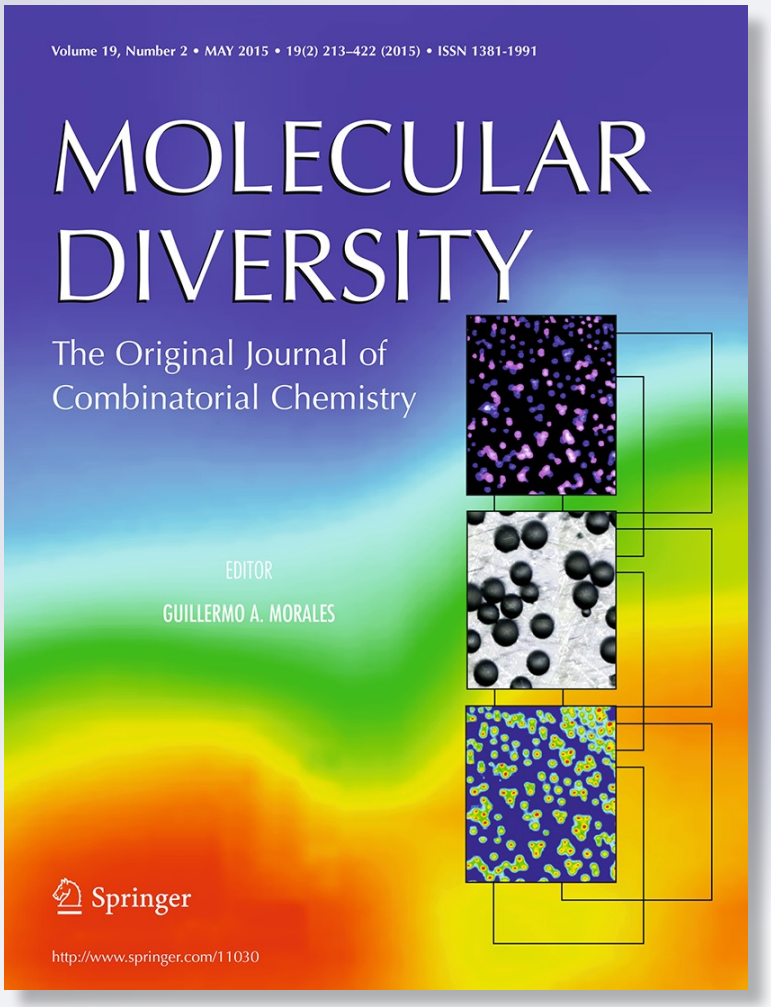
One-step synthesis of azole- and benzazole-based sulfonamides in aqueous media

Hassan Zali-Boeini, Zhaleh Najafi, Bahareh Abtahi & Hajar Golshadi Ghaleshahi

Molecular Diversity

ISSN 1381-1991
Volume 19
Number 2

Mol Divers (2015) 19:283-292
DOI 10.1007/s11030-015-9567-5



Springer

Mol Divers (2015) 19:283–292
DOI 10.1007/s11030-015-9567-5

FULL-LENGTH PAPER

One-step synthesis of azole- and benzazole-based sulfonamides in aqueous media

Hassan Zali-Boeini · Zhaleh Najafi · Bahareh Abtahi · Hajar Golshadi Ghaleshahi

Received: 30 June 2014 / Accepted: 11 January 2015 / Published online: 23 January 2015

Abstract Several benzazoles (benzoxazoles, benzothiazoles, and benzimidazoles) and azoles (1*H*-1,2,4-triazole-5(4*H*)-thiones and 1,2,4-oxadiazoles) bearing a sulfonamide moiety were efficiently prepared via the reactions of dimethyl (arylsulfonyl) dithioimidocarbonate derivatives and their 2-aminobenzene precursors, thiosemicarbazides, and amidoximes, respectively, in the presence of K_2CO_3 as a base in aqueous ethanol (25 %) as a green media in moderate to excellent yields.

Keywords Azoles · Benzazoles · Sulfonamides · Heterocycles · Green chemistry

Introduction

It is well known that benzazoles (benzoxazoles, benzothiazoles, and benzimidazoles) and azoles (oxadiazoles and triazoles) are among the most important compounds in heterocyclic chemistry due to their broad applications in medicinal chemistry [1–12], material sciences [13,14], and industry [15–17]. They are also important structural moieties frequently found in natural products [18,19]. Meanwhile, the unique role of sulfonamides as effective compounds in drug development and as diuretic and antibiotic drugs is well known [20,21], and their representative applications in medicinal chemistry are shown in Fig. 1.

There are diverse methods for the construction of benzazoles. Among them, the cyclocondensation reaction of carboxylic acids, acid derivatives, or aldehydes with a suitable 2-amino precursor is more common [22–25]. Some of the most recent approaches for the preparation of benzazoles and aforesaid azoles have been reviewed in the literature [26–33]. Although a number of methods are currently being employed for the preparation of some heterocycles containing a sulfonamide moiety using dimethyl (arylsulfonyl) dithioimidocarbonates [34–39], as far as we know none of them involves the use of "green chemistry". They suffer from a number of drawbacks, including harsh reaction conditions (reaction temperature: 140–170 °C), less green solvents (ethylene glycol), difficult separation methods, and low product yields (10–69 %) often accompanied with longer reaction times (90–120 min).

Herein, we report an efficient one step, mild method for the synthesis of diverse benzazoles and azoles containing a sulfonamide functional group in aqueous media as an environmentally benign solvent.

Results and discussion

We began our study exploring the reaction of dimethyl (phenylsulfonyl) dithioimidocarbonate **1a** with 2-aminothiophenol **2a** which also functions as an aminobenzene precursor. Using K_2CO_3 as a base and DMF as solvent, the reaction proceeded smoothly at room temperature to produce the corresponding benzothiazole **3a** in 90 min albeit in low yield (43 %). Increasing the temperature to 85 °C improved notably the reaction yield and shortened reaction time (70 %, 60 min). We found that at higher temperatures some extents of tarry materials and/or colored impurities were produced. Next, we proceeded to investigate the reaction course using a safe and environmentally friendly solvent. First, when EtOH

Electronic supplementary material The online version of this article (doi:10.1007/s11030-015-9567-5) contains supplementary material, which is available to authorized users.

H. Zali-Boeini (✉) · Z. Najafi · B. Abtahi · H. G. Ghaleshahi
Department of Chemistry, University of Isfahan,
81746-73441 Isfahan, Iran
e-mail: h.zali@chem.ui.ac.ir

Fig. 1 Representative applications of heterocyclic sulfonamides

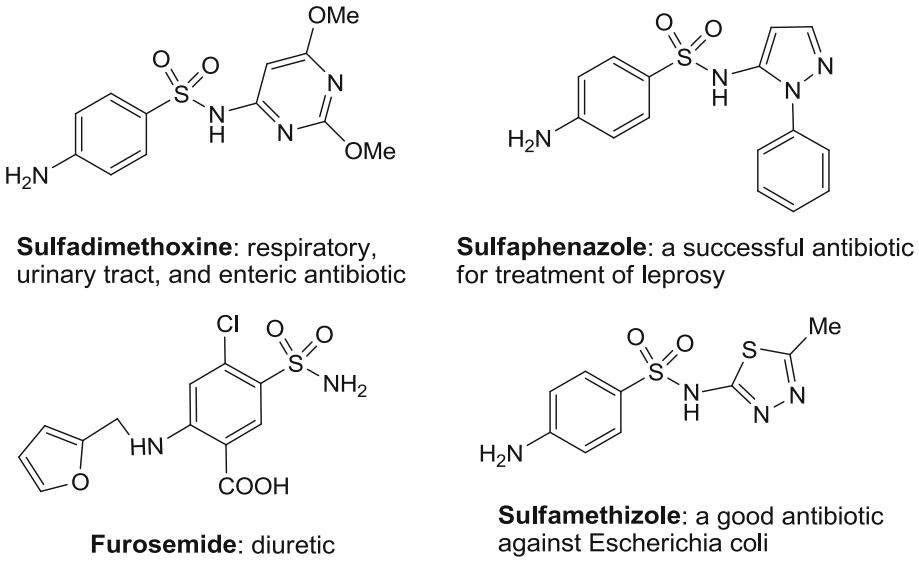


Table 1 Screening of solvent, temperature, and the reaction time in the synthesis of benzothiazole **3a**

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)[a]
1	DMF	rt	90	43
2	DMF	85	45	70
3	EtOH	80[b]	120	73
4	EtOH/H_2O (1:1), HTAB $_{cat}$	85[b]	60	86
5	EtOH/H_2O (1:2), HTAB $_{cat}$	85[b]	60	92
6	EtOH/H_2O (1:3), HTAB $_{cat}$	85[b]	60	95

2-Aminothiophenol **1a** (1 mmol), dimethyl phenylsulfonyl carbonimido-dithioate **2a** (1.1 mmol), K_2CO_3 (1.5 mmol, 0.2 g). [a] Isolated yields. [b] At reflux condition

was used as green solvent, benzothiazole **3a** was produced in slightly better yields, although the reaction time increased to 2 h. However, when a mixture of EtOH/H_2O was used along with a catalytic amount of hexadecyltrimethylammonium bromide (HTAB) the reaction yield increased significantly (86 %), while the reaction time was reduced to 1 h (Table 1). We found that the best solvent ratio and temperature to achieve optimum reaction conditions were 1:3 (EtOH/H_2O) at reflux temperature. Hence, a EtOH/H_2O (1:3)/$HTAB_{cat}$ system was chosen to carry out all our reactions under reflux conditions.

Fortunately, all dimethyl (arylsulfonyl) dithioimidocarbonates **1a**–**1d**, when treated with different types of 2-aminobenzene precursors **2a**–**2e**, were readily converted to their corresponding benzazoles bearing a sulfonamide functional group **3a**–**3k**. To expand the scope of our methodology, we next examined the reactions of dimethyl (arylsulfonyl) dithioimidocarbonates with different types of amino precursors, such as amidoximes and thiosemicarbazides (Scheme 1).

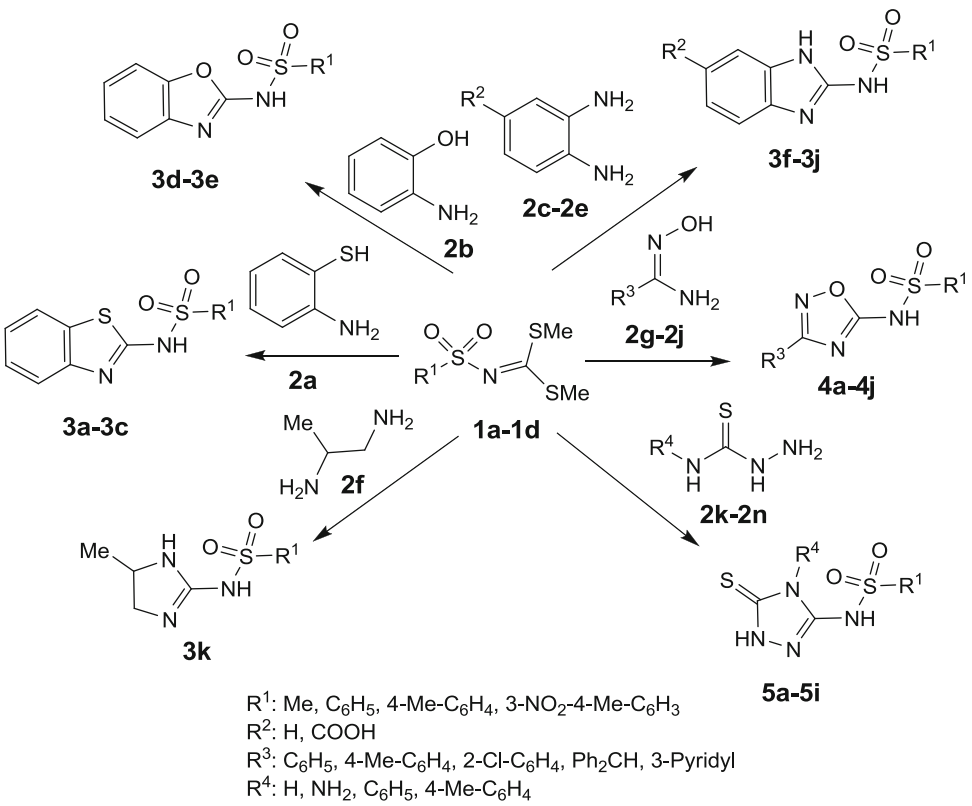
Utilizing the optimized reaction conditions, dimethyl (arylsulfonyl) dithioimidocarbonates **1a**–**1d** were treated with amidoximes **2g**–**2j** and thiosemicarbazides **2k**–**2n** to produce their corresponding 1,2,4-oxadiazole **4a**–**4j** and 1,2,4-triazole **5a**–**5i** derivatives, respectively, in good to excellent yields (69–91 %). The generality of the present method has been confirmed by the successful synthesis of several azole and benzazole derivatives (30 examples), and the results are summarized in Fig. 2.

Our proposed reaction mechanism for the formation of benzazoles **3** starts with the activation of amino precursor **2** by K_2CO_3 which then participate in a nucleophilic attack on the dimethyl (arylsulfonyl) dithioimidocarbonate **1** to give intermediate **6** after an addition-elimination type reaction releasing MeSH. Following cyclization and elimination of a further MeSH molecule, intermediate **7** is produced, which eventually aromatizes yielding the benzazole derivatives **3** (Scheme 2).

We found that all of the prepared sulfonamides containing oxadiazoles lacked the characteristic broad N–H sulfonamide proton signal around the 10–13 ppm region in the ^{1}H NMR spectrum. To evaluate this finding, the crystal structure of compound **4i** was determined (Fig. 3, CCDC 995893).

Unexpectedly, we found that compounds **4a**–**4j** were converted to their potassium salts and the corresponding supramolecular polymers through non-covalent interactions. These supramolecular polymers are most likely established via ion-ion, ion-dipole, cation-π, and π–π stacking interactions between deprotonated oxadiazole **4i** molecules and potassium cations in the crystal lattice (Fig. 4a, b).

Scheme 1 Synthetic approaches to several heterocyclic sulfonamides



Conclusions

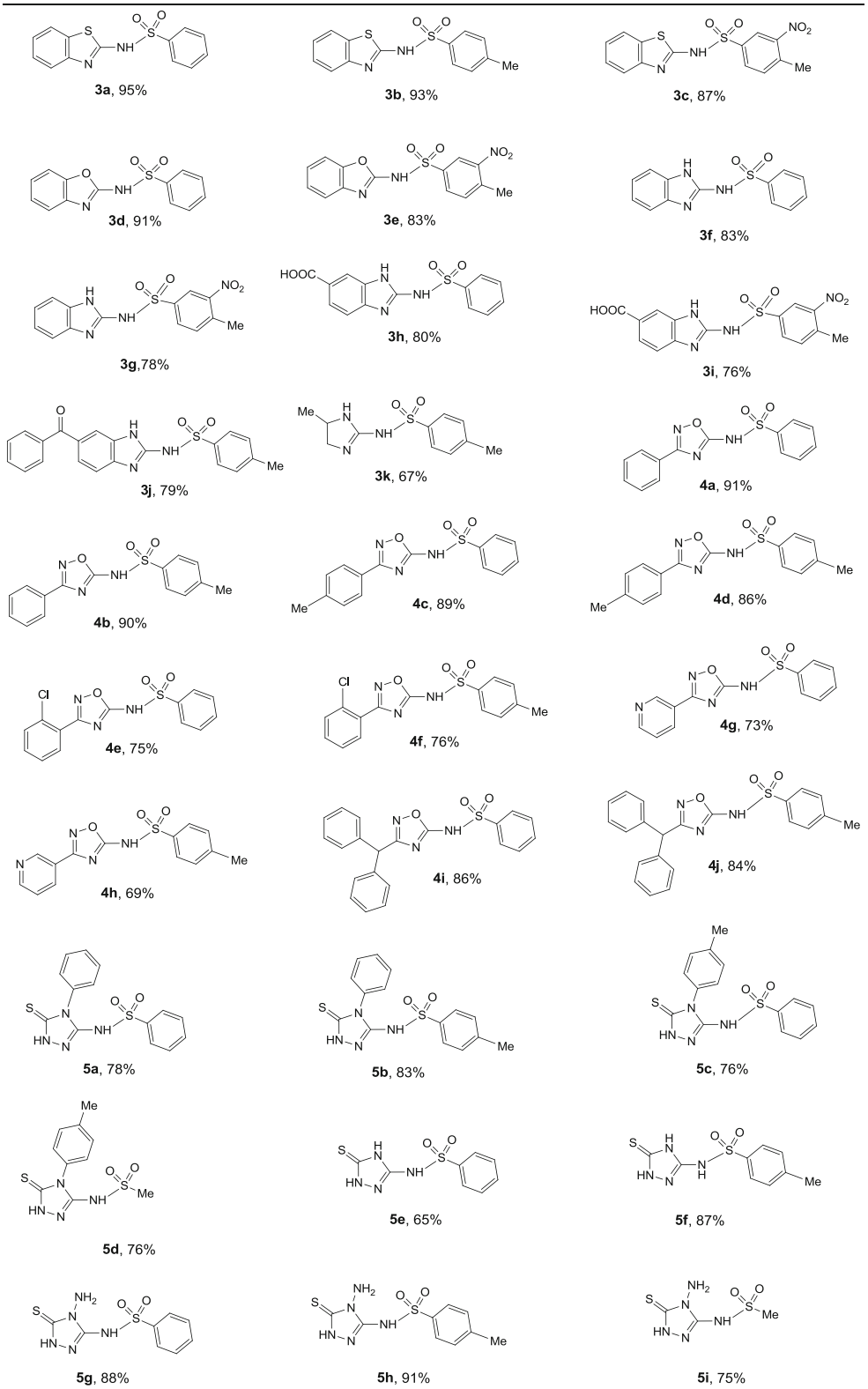
We developed an efficient one step and environmentally benign approach for the preparation of several new benzoxazoles, benzothiazoles, benzimidazoles, 1*H*-1,2,4-triazole-5(4*H*)-thiones, and 1,2,4-oxadiazoles containing a sulfonamide moiety. Simultaneous construction of heterocyclic rings and the sulfonamide moiety is one of the most prominent features of the present method. Performing the reactions in a very safe and environmentally benign solvent system is still another advantage of the method. Surprisingly, isolation and the purification of the final products were very simple with no needs for utilizing tedious and time-consuming separation technic such as column chromatography. Considering the biological and pharmaceutical importance of the heterocyclic sulfonamides, the present method could be a useful alternative for the synthesis of such valuable compounds in only one step using cheap and readily available starting materials.

Experimental section

All reagents, unless otherwise stated, were used as received from commercial suppliers. Melting points were determined with a Stuart Scientific SMP2 apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on UV-active aluminum-backed plates of silica gel (TLC Silica gel 60 F_{254}). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using $(CD_3)_2SO$ as the solvent referenced to a residual solvent protons, and signals are reported in ppm (δ) using s, d, t, and m abbreviations to show the relevant multiplicities as singlet, doublet, triplet, and multiplet, respectively. Elemental analysis was done on a LECO CHNS-932 analyzer.

General procedure for the synthesis of benzazoles (benzoxazoles, benzothiazoles, and benzimidazoles) bearing a sulfonamide moiety in 2-position

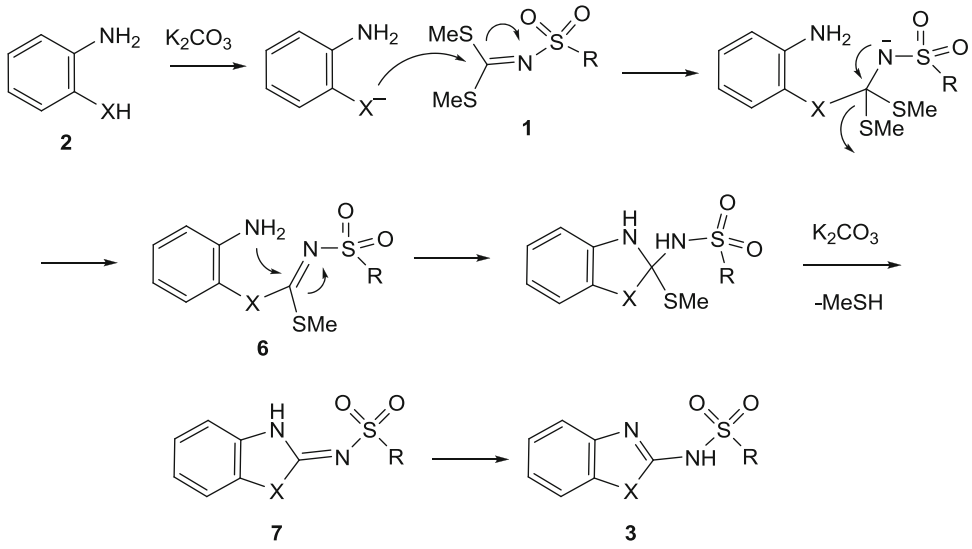
To a warm (40 °C) mixture of 2-amino precursor (2-aminothiophenol, 2-aminophenol, or 1,2-diaminobenzene **2a**–**2e**, 1 mmol), K_2CO_3 (1.5 mmol, 0.2 g), and hexadecyltrimethylammonium bromide (HTAB, 0.1 mmol, 36.5 mg) in H_2O/EtOH (3:1, 4 mL), dimethyl (arylsulfonyl) dithioimidocarbonate **1** (1.1 mmol) was added under stirring, and then heated to reflux for 60 min. After cooling to room temperature, the reaction mixture was poured onto cold water (6 mL) and stirred with diethyl ether (15 mL) to precipitate the crude product as off-white solid. The resulting crude residue was filtered and recrystallized from EtOH to obtain pure benzothiazoles, benzoxazoles, and benzimidazole derivatives **3** as white crystals.



[a] Dimethyl (arylsulfonyl) dithioimidocarbonate 1 (1.1 mmol), amino precursor 2 (1 mmol), EtOH/H_2O (1:3, 5mL), K_2CO_3 (1.5 mmol), HTAB (20 mg).

Fig. 2 One-step synthesis of diverse heterocyclic sulfonamides in aqueous medium. *Note* Dimethyl (arylsulfonyl) dithioimidocarbonate 1 (1.1 mmol), amino precursor 2 (1 mmol), EtOH/H_2O (1:3, 5 mL), K_2CO_3 (1.5 mmol), HTAB (20 mg)

Scheme 2 Proposed reaction mechanism for the formation of **3**



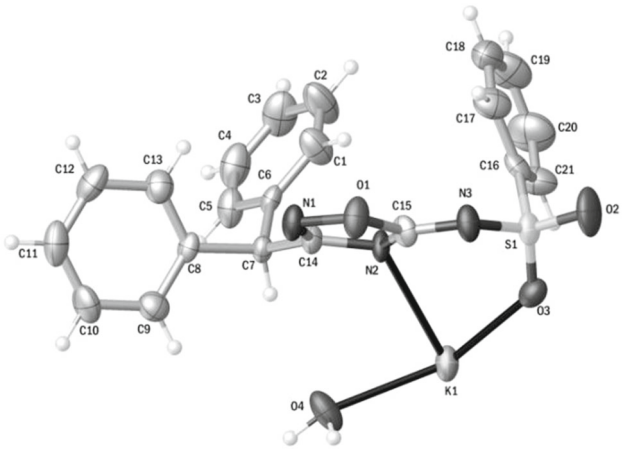


Fig. 3 ORTEP view of the asymmetric unit of the compound **4i**. Non-H atoms represented as displacement ellipsoids are plotted at the 50 % probability level, while H atoms are shown as small spheres of arbitrary radius

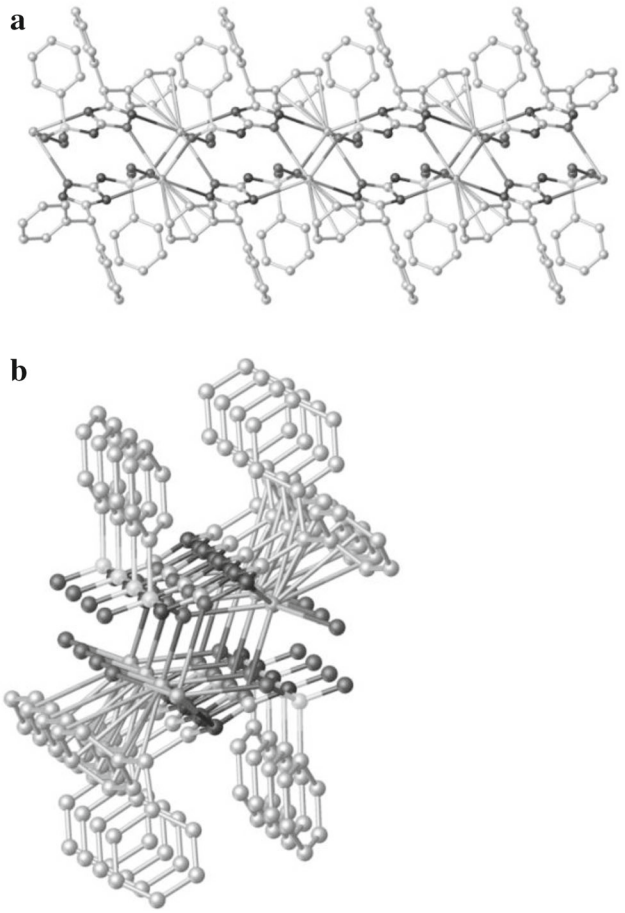


Fig. 4 **a** Side view of one-dimensional polymeric chain of compound **4i** extending along the crystallographic *b* axis. **b** Side view of one-dimensional polymeric chain of the compound along the crystallographic *a* axis, H atoms have been omitted for clarity

General procedure for the synthesis of 1,2,4-oxadiazoles bearing a sulfonamide moiety in 5-position

To a stirred warm (40 °C) mixture of amidoximes **2f**–**2i** (1 mmol), K_2CO_3 (1.5 mmol, 0.2 g), and hexadecyltrimethylammonium bromide (HTAB, 0.1 mmol, 36.5 mg) in H_2O/EtOH (3:1, 8 mL), dimethyl (arylsulfonyl) dithioimidocarbonate **1** (1.1 mmol) was added under stirring, and then heated to reflux for 60 min. Then the reaction mixture was cooled and the precipitated product was stirred with EtOAc (10 mL) to deposit the crude residue as white solid. Finally, the crude residue was filtered and recrystallized from EtOH to obtain pure white crystals of 1,2,4-oxadiazoles **4** as potassium salts.

General procedure for the synthesis of 1,2,4-triazoles bearing a sulfonamide moiety in 3-position

A suspension mixture of thiosemicarbazides **2j**–**2m** (1 mmol), K_2CO_3 (1.5 mmol, 0.2 g), and hexadecyltrimethylammonium bromide (HTAB, 0.1 mmol, 36.5 mg) in H_2O (6 ml) was added under stirring to a solution of dimethyl (arylsulfonyl) dithioimidocarbonate**1** (1.1 mmol) in EtOH (2 mL). Then, the reaction mixture was stirred and heated to reflux for 60 min. After cooling to room temperature, the off-white precipitated residue was filtered and stirred with EtOAc (10 mL) to deposit a white residue. Finally, the crude product was filtered and recrystallized from EtOH to obtain pure 1,2,4-triazoles **5** as white needles.

*N-(benzo[d]thiazol-2-yl)benzenesulfonamide (**3a**)*

m.p. 218–219 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.17 (s, 1H), 7.80 (d, J = 8.0, 1H), 7.75 (d, J = 8.0, 2H), 7.24–7.39 (m, 5H), 2.36 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 167.0, 141.9, 136.1, 132.4, 129.1, 127.3, 125.8, 124.7, 123.6, 122.7, 112.8; Anal. Calcd. for $C_{13}H_{10}N_2O_2S_2$: C, 53.77; H, 3.47; N, 9.65; S, 22.09 Found: C, 53.74; H, 3.45; N, 9.70; S, 22.12.

*N-(benzo[d]thiazol-2-yl)-4-methylbenzenesulfonamide (**3b**)*

m.p. 229–231 °C (dc) ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.18 (s, 1H), 7.84–7.88 (m, 3H), 7.55–7.63 (m, 3H), 7.24–7.41 (m, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 156.0, 144.4, 142.2, 132.2, 130.0, 129.9, 126.6, 125.5, 123.6, 111.2, 110.0, 19.5; Anal. Calcd. for $C_{14}H_{12}N_2O_2S_2$: C, 55.24; H, 3.97; N, 9.20; S, 21.07 Found: C, 55.17; H, 3.89; N, 9.24; S, 21.01.

*N-(benzo[d]thiazol-2-yl)-4-methyl-3-nitrobenzenesulfonamide (**3c**)*

m.p. 245–247 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.42 (s, 1H), 8.07 (dd, J = 8.0, 1H), 7.84 (d, J= 8.0, 1H), 7.71 (d, J = 8.0, 1H), 7.26–7.43 (m, 4H), 2.57 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 156.9, 148.5, 144.7, 141.6, 137.1, 133.8, 130.4, 125.1, 125.0 123.2, 122.3, 112.4, 110.1, 19.6; Anal. Calcd. for $C_{14}H_{11}N_3O_4S_2$: C, 48.13; H, 3.17; N, 12.03; S, 18.36 Found: C, 48.04; H, 3.13; N, 12.13; S, 18.29.

*N-(benzo[d]oxazol-2-yl)benzenesulfonamide (**3d**)*

m.p. 210–211 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.81 (s, 1H), 7.21–7.95 (m, 9H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 156.0, 144.1, 142.3, 132.4, 129.8, 129.0, 126.0, 125.3, 123.6, 111.9, 110.3; Anal. Calcd. for $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69 Found: C, 56.88; H, 3.63; N, 10.25; S, 11.65.

*N-(benzo[d]oxazol-2-yl)-4-methyl-3-nitrobenzenesulfonamide (**3e**)*

m.p. 237–238 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.97 (s,1H), 8.14 (d, J = 8.0, 1H), 7.70 (d, J = 8.0, 1H), 7.49 (d, J = 4.0, 1H), 7.19–7.34 (m, 4H), 2.57 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 167.6, 148.5, 141.0, 137.4, 136.5, 134.0, 129.9, 127.3, 124.9, 123.8, 122.8, 121.8, 113.1, 19.6; Anal. Calcd. for $C_{14}H_{11}N_3O_5S$: C, 50.45; H, 3.33; N, 12.61; S, 9.62 Found: C, 50.48; H, 3.30; N, 12.64; S, 9.66.

*N-(1H-benzo[d]imidazol-2-yl)benzenesulfonamide (**3f**)*

m.p. 240–242 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 11.96 (s, 2H), 7.90 (d, J = 8.0, 2H), 7.53 (d, J = 4.0, 3H), 7.29 (m, 2H), 7.13 (q, J = 4.0, 2H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 149.8, 144.0, 131.5, 129.3, 128.8, 125.5, 122.4, 110.9; Anal. Calcd. for $C_{13}H_{11}N_3O_2S$: C, 57.13; H, 4.06; N, 15.37; S, 11.73 Found: C, 57.01; H, 3.98; N, 15.30; S, 11.82.

*N-(1H-benzo[d]imidazol-2-yl)- 4-methyl-3-nitro benzenesulfonamide (**3g**)*

m.p. 249–251 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.11 (s, 2H), 8.44 (s, 1H), 8.10 (s, 1H), 7.67 (d, J = 8.0, 1H), 7.30 (d, J = 8.0, 2H), 7.14–7.16 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 155.9, 144.1, 142.3, 136.5, 133.8, 129.8, 129.3, 122.7, 121.6, 111.1, 19.6; Anal. Calcd. for $C_{14}H_{12}N_4O_4S$: C, 50.60; H, 3.64; N, 16.86; S, 9.65 Found: C, 50.63; H, 3.60; N, 16.89; S, 9.59.

*2-(Phenylsulfonamido)-1H-benzo[d]imidazole-6-carboxylic acid (**3h**)*

m.p. 242–243 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.79 (s, 1H), 12.22 (s, 2H), 7.76–7.91 (m, 4H), 7.51–7.57 (m, 3H), 7.33 (d, J = 8.0, 1H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 167.1, 150.7, 143.7, 132.9, 131.6, 129.4, 128.9, 125.5, 124.9, 124.4, 112.0, 110.5; Anal. Calcd. for $C_{14}H_{11}N_3O_4S$: C, 52.99; H, 3.49; N, 13.24; S, 10.10 Found: C, 52.95; H, 3.47; N, 13.29; S, 10.16.

*2-(4-methyl-3-nitrophenylsulfonamido)-1H-benzo[d]imidazole-6-carboxylic acid (**3i**)*

m.p. 248–250 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.42 (s, 1H), 12.11 (s, 1H), 8.44 (s, 1H), 8.08 (q, J = 4.0, 1H), 7.67 (d, J = 8.0, 1H), 7.30 (q, J = 4.0, 2H),

7.14–7.16 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 167.0, 156.0, 150.6, 142.7, 136.7, 133.9, 132.9, 129.8, 129.4, 125.1, 124.5, 121.7, 112.2, 110.7, 19.5; Anal. Calcd. for $C_{15}H_{12}N_4O_6S$: C, 47.87; H, 3.21; N, 14.89; S, 8.52 Found: C, 47.79; H, 3.16; N, 14.91; S, 8.60.

N - (6-benzoyl - 1H - benzo[d]imidazol - 2-yl) - 4 - methyl-benzenesulfonamide (**3j**)

m.p. 241–243 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.12 (s, 1H), 7.91 (d, J = 8.0, 2H), 7.65–7.71 (m, 4H), 7.50–7.58 (m, 6H), 7.37 (d,J = 8.0, 1H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 206.5, 194.9, 151.7, 144.0, 137.9, 134.6, 131.4, 130.6, 130.3, 129.3, 128.8, 128.4, 125.6, 125.0, 112.8, 110.7, 30.65; Anal. Calcd. for $C_{21}H_{17}N_3O_3S$: C, 64.43; H, 4.38; N, 10.73; S, 8.19 Found: C, 64.35; H, 4.33; N, 10.77; S, 8.13.

4 - Methyl - N -(5-methyl-4,5-dihydro-1H-imidazol-2-yl) benzenesulfonamide (**3k**)

m.p. 222–223 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.67 (s, 1H), 7.65 (d, J = 8.0, 2H), 7.43 (s, 1H), 7.30 (d, J = 8.0, 2H), 3.82–3.87 (m, 1H), 3.55 (t, J = 12.0, 1H), 2.98 (dd, J = 4.0, 4.0, 1H), 2.35 (s, 3H), 1.11 (d, J = 4.0, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 159.4, 141.5, 141.2, 129.0, 125.6, 49.4, 48.6, 20.9, 20.6; Anal. Calcd. for $C_{11}H_{15}N_3O_2S$: C, 52.15; H, 5.97; N, 16.59; S, 12.66 Found: C, 52.12; H, 5.94; N, 16.61; S, 12.68.

Potassium (3- phenyl- 1,2,4- oxadiazol- 5- yl)(phenyl-sulfonyl)amide (**4a**)

m.p. 208–210 °C; IR (KBr) υ: 3032, 3058, 1549, 1444, 1384, 1261, 1137, 1092, 936, 786,755, 688 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.89–7.91 (m, 2H, CH_{arom}), 7.79–7.82 (m, 2H, CH_{arom}), 7.43–7.47 (m, 6H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.63, 166.98, 144.87, 130.24, 130.01, 128.89, 128.59, 127.78, 126.79, 126.25; Anal. Calcd. for $C_{14}H_{10}KN_3O_3S$: C, 49.54; H, 2.97; N, 12.38; S, 9.45 Found: C, 49.44; H, 2.89; N, 12.40; S, 9.41.

Potassium (3-phenyl-1,2,4-oxadiazol-5-yl)(tosyl)amide (**4b**)

m.p. 210–211 °C; IR (KBr) $\upsilon_{C=N}$: 3074, 2926, 2857, 1639, 1595, 1472,1339, 1319,1148,1089, 886, 739 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.86 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{arom}), 7.52–7.60 (m, 3H, CH_{arom}), 7.40 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 2.37 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.45, 163.94, 143.12, 138.15, 131.73, 129.37, 129.10, 127.04, 126.73, 124.98, 20.98; Anal. Calcd. for $C_{15}H_{12}KN_3O_3S$: C, 50.97; H, 3.42; N, 11.89; S, 9.07 Found: C, 50.85; H, 3.39; N, 11.99; S, 9.09.

Potassium (3 - p - tolyl - 1,2,4 - oxadiazol - 5 - yl) (phenylsulfonyl)amide (**4c**)

m.p. 218–220 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.87–7.90 (m, 2H, CH_{arom}), 7.69 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 7.41–7.44 (m, 3H, CH_{arom}), 7.25 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.59, 166.94, 144.98, 139.57, 130.17, 129.12, 128.63, 127.75, 126.77, 126.21, 20.97; Anal. Calcd. for $C_{15}H_{12}KN_3O_3S$: C, 50.97; H, 3.42; N, 11.89; S, 9.07 Found: C, 50.89; H, 3.36; N, 11.93; S, 9.01.

Potassium (3-p-tolyl-1,2,4-oxadiazol-5-yl)(tosyl)amide (**4d**)

m.p. 220–222 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 7.70 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH_{arom}), 7.21–7.26 (m, 4H, CH_{arom}), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.53, 166.92, 142.16, 139.91, 139.56, 129.26, 129.12, 128.19, 126.85, 126.21, 20.97, 20.83; Anal. Calcd. for $C_{16}H_{14}KN_3O_3S$: C, 52.30; H, 3.84; N, 11.44; S, 8.73 Found: C, 52.20; H, 3.78; N, 11.49; S, 8.81.

Potassium (3-(2-chlorophenyl)-1,2,4-oxadiazol-5-yl) (phenylsulfonyl)amide (**4e**)

m.p. 205–208 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.87–7.90 (m, 2H, CH_{arom}), 7.68–7.71 (m, 1H, CH_{arom}), 7.53–7.55 (m, 1H, CH_{arom}), 7.40–7.49 (m, 5H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.18, 166.21, 144.81, 131.19, 131.11, 130.36, 130.28, 129.75, 127.82, 127.62, 127.10, 126.74; Anal. Calcd. for $C_{14}H_9ClKN_3O_3S$: C, 44.98; H, 2.43; N, 11.24; S, 8.58 Found: C, 44.84; H, 2.38; N, 11.26; S, 8.53.

Potassium (3-(2-chlorophenyl)-1,2,4-oxadiazol-5-yl) (tosyl)amide (**4f**)

m.p. 207–209 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.78 (d, $^3J_{HH}$ = 8.4 Hz, 2H, CH_{arom}), 7. 70–7.72 (m, 1H, CH_{arom}), 7.53–7.55 (dd, $^3J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 7.8 Hz, 1H, CH_{arom}), 7.41–7.49 (m, 2H, CH_{arom}), 7.22 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 2.32 (s, 3H, CH_3),; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.15, 166.16, 142.11, 139.98, 131.68, 131.57, 131.21, 131.06, 130.36, 128.25, 127.09, 126.79, 20.84; Anal. Calcd. for $C_{15}H_{11}ClKN_3O_3S$: C, 46.45; H, 2.86; N, 10.83; S, 8.27 Found: C, 46.37; H, 2.81; N, 10.89; S, 8.24.

*Potassium (3-(pyridin-3-yl)-1,2,4-oxadiazol-5-yl) (phenylsulfonyl)amide (**4g**)*

m.p. 283–286 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.95 (s, 1H, CH_{arom}), 8.65 (d, $^3J_{HH}$ = 4 Hz, 1H, CH_{arom}), 8.12 (d, $^3J_{HH}$ = 8 Hz, 1H, CH_{arom}), 7.90 (d, $^3J_{HH}$ = 1.6 Hz, 2H, CH_{arom}), 7.44–7.51 (m, 4H, CH_{arom}); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 178.0, 165.2, 150.9, 149. 8, 147.2, 146.8, 133.7, 130.3, 127.8, 126.8, 123.9; Anal. Calcd. for $C_{13}H_9KN_4O_3S$: C, 45.87; H, 2.66; N, 16.46; S, 9.42 Found: C, 45.76; H, 2.61; N, 16.51; S, 9.39.

*Potassium (3-(pyridin-3-yl)-1,2,4-oxadiazol-5-yl)(tosyl) amide (**4h**)*

m.p. 285–288 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.96 (d, $^3J_{HH}$ = 1.6 Hz, 2H, CH_{arom}), 8.64–8.66 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 1.6 Hz, 1H, CH_{arom}), 8.11–8.15 (td, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 2 Hz, 1H, CH_{arom}), 7.78 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 7.48–7.51 (m, 1H, CH_{arom}), 7.24 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH_{arom}), 2.32 (s,3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.77, 165.16, 150.93, 147.18, 141.92, 140.08, 133.66, 128.26, 126.87, 124.84, 123.87, 20.84; Anal. Calcd. for $C_{14}H_{11}KN_4O_3S$: C, 47.44; H, 3.13; N, 15.81; S, 9.05 Found: C, 47.30; H, 3.04; N, 15.85; S, 9.12.

*Potassium (3-benzhydryl-1,2,4-oxadiazol-5-yl) (phenylsulfonyl)amide (**4i**)*

m.p. 186–188 °C; IR (KBr) υ: 3056, 3029, 3088, 3004, 2899, 1628, 1558, 1528, 1492, 1446, 1385, 1263, 1149, 1073, 941, 844,787, 751, 693 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.84–7.87 (m, 2H, CH_{arom}), 7.19–7.48 (m, 13H, CH_{arom}), 5.19 (s, 1H, CH_{benzyl}); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.5, 170.3, 144.8, 141.2, 130.1, 128.5, 128.1, 127.7, 126.8, 126.4, 48.1; Anal. Calcd. for $C_{21}H_{16}KN_3O_3S$: C, 58.72; H, 3.75; N, 9.78; S, 7.47 Found: C, 58.68; H, 3.69; N, 9.82; S, 7.41.

*Potassium (3-benzhydryl-1,2,4-oxadiazol-5-yl)(tosyl) amide (**4j**)*

m.p. 191–194 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.71 (d, $^3J_{HH}$ = 8 Hz, 2H, CH_{arom}), 7.19–7.34 (m, 12H, CH_{arom}), 5.17 (s, 1H, CH_{benzyl}), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 172.4, 170.2, 142.1, 141.3, 129.3, 128.5, 128.2, 128.1, 126.9, 126.4, 48.1, 20.9; Anal. Calcd. for $C_{22}H_{18}KN_3O_3S$: C, 59.57; H, 4.09; N, 9.47; S, 7.23 Found: C, 59.51; H, 4.02; N, 9.52; S, 7.26.

*N-(4-phenyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl) benzenesulfonamide (**5a**)*

m.p. 303–307 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.39 (s, 1H), 10.10 (s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.54–7.63 (m, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 8.4 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 162.5, 153.2, 142.6, 139.9, 132.1, 129.1, 129.1, 125.6, 122.0, 117.3; Anal. Calcd. for $C_{14}H_{12}N_4O_2S_2$: C, 50.59; H, 3.64; N, 16.86; S, 19.29 Found: C, 50.51; H, 3.58; N, 16.90; S, 19.23.

*4-Methyl-N-(4-phenyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)benzenesulfonamide (**5b**)*

m.p. 317–318 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.77 (s, 1H), 10.11 (s, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.53–7.57 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.30 (d, $^3J_{HH}$ = 6.4 Hz, 2H), 7.00 (t, J = 7.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 167.3, 153.3, 143.6, 137.5, 132.6, 129.6, 129.3, 129.0, 128.4, 126.9, 21.0; Anal. Calcd. for $C_{15}H_{14}N_4O_2S_2$: C, 52.01; H, 4.07; N, 16.17; S, 18.51 Found: C, 51.94; H, 4.01; N, 16.11; S, 18.57.

*N-(5-thioxo-4-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-3-yl)benzenesulfonamide (**5c**)*

m.p. 313–316 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.55 (s, 1H), 9.99 (s, 1H), 7.79 (d, J = 7.2 Hz, 2H), 7.53–7.61 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 162.4, 153.3, 142.6, 137.4, 132.1, 131.0, 129.5, 129.1, 125.5, 117.5, 20.3; Anal. Calcd. for $C_{15}H_{14}N_4O_2S_2$: C, 52.01; H, 4.07; N, 16.17; S, 18.51 Found: C, 51.98; H, 3.98; N, 16.14; S, 18.54.

*N-(5-thioxo-4-p-tolyl-4,5-dihydro-1H-1,2,4-triazol-3-yl)methanesulfonamide (**5d**)*

m.p. 287–289 °C (dc); ^{1}H NMR (DMSO-d_6, 400MHz) δ: 13.93 (s, 1H), 8.67 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 2.79 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 166.2, 142.1, 138.4, 131.6, 129.5, 125.6, 37.4, 20.7; Anal. Calcd. for $C_{10}H_{12}N_4O_2S_2$: C, 42.24; H, 4.25; N, 19.70; S, 22.55 Found: C, 42.16; H, 4.21; N, 19.75; S, 22.61.

*N-(5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)benzenesulfonamide (**5e**)*

m.p. 301–303 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 12.88 (s, 1H), 8.27 (s, 1H), 7.95 (d, J = 7.20 Hz, 2H), 7.54–7.60 (m, 3H), 7.04 (s, 1H); ^{13}C NMR (DMSO-d_6, 400 MHz)

δ: 163.1, 157.7, 142.8, 131.9, 129.0, 126.1; Anal. Calcd. for $C_8H_8N_4O_2S_2$: C, 37.49; H, 3.15; N, 21.86; S, 25.02 Found: C, 37.41; H, 3.09; N, 21.80; S, 25.11.

*4-Methyl-N-(5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)benzenesulfonamide (**5f**)*

m.p. 311–313 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHZ) δ: 13.05 (s, 1H), 8.26 (s, 1H), 8.00 (s, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 161.5, 150.7, 142.6, 139.3, 129.4, 126.2, 20.9; Anal. Calcd. for $C_9H_{10}N_4O_2S_2$: C, 39.99; H, 3.73; N, 20.73; S, 23.72 Found: C, 39.83; H, 3.66; N, 20.71; S, 23.82.

*N-(4-amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl) benzenesulfonamide (**5g**)*

m.p. 297–300 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.43 (s, 1H), 10.15 (s, 1H), 7.93 (d, J = 7.20 Hz, 2H), 7.69-7.72 (m, 1H), 7.61–7.65 (m, 2H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 165.6, 143.8, 140.1, 133.3, 129.1, 127.0; Anal. Calcd. for $C_8H_9N_5O_2S_2$: C, 35.41; H, 3.34; N, 25.81; S, 23.64 Found: C, 35.30; H, 3.27; N, 25.75; S, 23.72.

*N-(4-amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl) -4-methylbenzenesulfonamide (**5h**)*

m.p. 317–319 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.41 (s, 1H), 10.29 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.29 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 165.5, 143.8, 141.8, 137.2, 129.5, 127.1, 21.0; Anal. Calcd. for $C_9H_{11}N_5O_2S_2$: C, 37.88; H, 3.89; N, 24.54; S, 22.47 Found: C, 37.79; H, 3.82; N, 24.51; S, 22.51.

*N-(4-amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl) methanesulfonamide (**5i**)*

m.p. 258–260 °C (dc); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.70 (s, 1H), 8.45 (s, 1H,), 5.71 (s, 2H), 2.80 (s, 3H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ: 165.5, 142.0, 36.1; Anal. Calcd. for $C_3H_7N_5O_2S_2$: C, 17.22; H, 3.37; N, 33.47; S, 30.65 Found: C, 17.11; H, 3.32; N, 33.51; S, 30.58.

For full experimental procedure, ^{1}H NMR and ^{13}C NMR spectral data (including their copies) for all compounds see the provided supplementary material.

Acknowledgments We warmly thank the University of Isfahan research council for financial support of this work.

References

1. Deluca MR, Kerwin SM (1997) The total synthesis of UK-1. Tetrahedron Lett 38:199–202. doi:10.1016/S0040-4039(96)02288-5
2. Sato Y, Yamada M, Yoshida S, Soneda T, Ishikawa M, Nizato T, Suzuki K, Konno F (1998) Benzoxazole derivatives as novel 5-HT3 receptor partial agonists in the gut. J Med Chem 41:3015–3021. doi:10.1021/jm9801004
3. Hutchinson I, Jenninga SA, Vishnuvajjala BR, Westwell AD, Stevens MFG (2002) Antitumor benzothiazoles. Synthesis and pharmaceutical properties of antitumor 2-(4-aminophenyl) benzothiazole amino acid prodrugs. J Med Chem 45:744–747. doi:10.1021/jm011025r
4. Yamamoto K, Fujita M, Tabashi K, Kawashima Y, Kato E, Oya M, Iso T, Iwao J (1988) Novel calcium antagonists. Synthesis and structure-activity relationship studies of benzothiazoline derivatives. J Med Chem 31:919–930. doi:10.1021/jm00400a006
5. Manas ES, Unwalla RJ, Xu ZB, Malamas MS, Miller CP, Harris HA, Hsiao C, Akopian T, Hum WT, Malakian K, Wolfrom S, Bapat A, Bhat RA, Stahl ML, Somers WS, Alvarez JC (2004) Structure-based design of estrogen receptor-β selective ligands. J Am Chem Soc 126:15106–15119. doi:10.1021/ja047633o
6. Malamas MS, Manas ES, McDevitt RE, Gunawan I, Xu ZB, Collini MD, Miller CP, Dinh T, Henderson RA, KeithJr JC, Harris HA (2004) Design and synthesis of aryl diphenolic azoles as potent and selective estrogen receptor-β ligands. J Med Chem 47:5021–5040. doi:10.1021/jm049719y
7. Aiello S, Wells G, Stone EL, Kadri H, Bazzi R, Bell DR, Stevens MFG, Matthews CS, Bradshaw TD, Westwell AD (2008) Synthesis and biological properties of benzothiazole, benzoxazole, and chromen-4-one analogues of the potent antitumor agent 2-(3,4-dimethoxyphenyl)-5-fluorobenzothiazole (PMX 610, NSC 721648). J Med Chem 51:5135–5139. doi:10.1021/jm800418z
8. Temiz O, Oren I, Sener E, Yalcin I, Ucarturk N (1998) Synthesis and microbiological activity of some novel 5- or 6-methyl-2-(2,4-disubstituted phenyl) benzoxazole derivatives. Farmaco 53:337–341. doi:10.1016/S0014-827X(98)00030-5
9. Tron GC, Pirali T, Billington RA, Canonico PL, Sorba G, Genazzani AA (2008) Click chemistry reactions in medicinal chemistry: applications of the 1,3-dipolar cycloaddition between azides and alkynes. Med Res Rev 28:278–308. doi:10.1002/med.20107
10. Whiting M, Muldoon J, Lin YC, Silverman SM, Lindstrom W, Olson AJ, Kolb HC, Finn MG, Sharpless KB, Elder JH, Fokin VV (2006) Inhibitors of HIV-1 protease by using in situ click chemistry. Angew Chem Int Ed 45:1435–1439. doi:10.1002/anie02161
11. Orlek BS, Blaney FE, Brown F, Clark MSG, Hadley MS, Hatcher J, Riley GJ, Rosenberg HE, Wadsorth HJ, Wyman PJ (1991) Comparison of azabicyclic esters and oxadiazoles as ligands for the muscarinic receptor. J Med Chem 34:2726–2735. doi:10.1021/jm00113a009
12. Swain CJ, Baker R, Kneen C, Moseley J, Saunders J, Seward EM, Stevenson G, Beer M, Stanton J, Watling KJ (1991) Novel 5-HT3 antagonists. Indole oxadiazoles. J Med Chem 34:140–151. doi:10.1021/jm00105a021
13. Ye CF, Gard GL, Winter RW, Syvret RG, Twamley B, Shreeve JM (2007) Synthesis of pentafluorosulfanylpyrazole and pentafluorosulfanyl-1,2,3-triazole and their derivatives as energetic materials by click chemistry. Org Lett 9:3841–3844. doi:10.1021/ol701602a
14. Nandivada H, Jiang XW, Lahann J (2007) Click chemistry: versatility and control in the hands of materials scientists. Adv Mater 19:2197–2208. doi:10.1002/adma.200602739
15. Zhang XH, Wong OY, Gao ZQ, Lee CS, Kwong HL, Lee ST, Wu SK (2001) A new blue-emitting benzothiazole derivative for organic

electroluminescent devices. Mater Sci Eng B 85:182–185. doi:10.1016/S0921-5107(01)00607-9
16. Mike JF, Makowski AJ, Jeffries-EL M (2008) An efficient synthesis of 2,6-disubstituted benzobisoxazoles: new building blocks for organic semiconductors. Org Lett 10:4915–4918. doi:10.1021/ol802011y
17. Heynderickx A, Guglielmetti R, Dubest R, Aubard J, Samat A (2003) Sulfinyl- and sulfonyl-substituted 2-benzylbenzoxazoles and 2-benzylbenzothiazoles as potential photochromic compounds. Synthesis 2003:1112–1116. doi:10.1055/s-2003-39178
18. Carbone M, Li Y, Irace C, Mollo E, Castelluccio F, Di Pascale A, Cimino G, Santamaria R, Guo Y, Gavagnin M (2011) Structure and cytotoxicity of phidianidines A and B: first finding of 1,2,4-oxadiazole system in a marine natural product. Org Lett 13:2516–2519. doi:10.1021/ol200234r
19. Rodríguez AD, Ramírez C, Rodríguez II, González E (1999) Novel antimycobacterial benzoxazole alkaloids, from the West Indian Sea whip Pseudopterogorgia elisabethae. Org Lett 1:527–530. doi:10.1021/ol9907116
20. Price CC, Reitsema RH (1947) Some sulfonamide derivatives of 2-aminobenzimidazole. J Org Chem 12:269–274. doi:10.1021/jo01166a010
21. Eidam O, Romagnoli C, Caselli E, Babaoglu K, Pohlhaus DT, Karpiak J, Bonnet R, Shoichet BK, Prati F (2010) Design, synthesis, crystal structures, and antimicrobial activity of sulfonamide boronic acids as β-lactamase Inhibitors. J Med Chem 53:7852–7863. doi:10.1021/jm101015z
22. Pottorf RS, Chadha NK, Katkevics M, Ozola V, Suna E, Ghane H, Regberg T, Player MR (2002) Parallel synthesis of benzoxazoles via microwave-assisted dielectric heating. Tetrahedron Lett 44:175–178. doi:10.1016/S0040-4039(02)02495-4
23. Varma RS, Saini RK, Prakash O (1997) Hypervalent iodine oxidation of phenolic schiff's bases: synthesis of 2-arylbenzoxazoles. Tetrahedron Lett 38:2621–2622. doi:10.1016/S0040-4039(97)00444-9
24. Kawashita Y, Nakamichi N, Kawabata H, Hayashi M (2003) Direct and practical synthesis of 2-arylbenzoxazoles promoted by activated carbon. Org Lett 5:3713–3715. doi:10.1021/ol035393w
25. Chen Y-X, Qian L-F, Zhang W, Han B (2008) Efficient aerobic oxidative synthesis of 2-substituted benzoxazoles, benzothiazoles, and benzimidazoles catalyzed by 4-methoxy-TEMPO. Angew Chem Int Ed Eng 47:9330–9333. doi:10.1002/anie.200803381
26. Bastug G, Eviolitte C, Markó IE (2012) Functionalized orthoesters as powerful building blocks for the efficient preparation of heteroaromatic bicycles. Org Lett 14:3502–3505. doi:10.1021/ol301472a
27. Yao W, Huang D (2010) Unexpected reactivity of o-nitrosophenol with RCH_2Br: C–H bond cleavage and annulation to benzoxazoles and benzoxazines. Org Lett 12:736–738. doi:10.1021/ol902812q
28. Chen C, Andreani T, Li H (2011) A divergent and selective synthesis of isomeric benzoxazoles from a single N–Cl imine. Org Lett 13:6300–6303. doi:10.1021/ol202844c
29. Marsden SP, McGonagle AE, McKeever-Abbas B (2008) Catalytic aza-Wittig cyclizations for heteroaromatic synthesis. Org Lett 10:2589–2591. doi:10.1021/ol800921n
30. Liao Y, Qi H, Chen S, Jiang P, Zhou W, Deng G (2012) Efficient 2-aryl benzothiazole formation from aryl ketones and 2-aminobenzenethiols under metal-free conditions. Org Lett 14:6004–6007. doi:10.1021/ol302902e
31. Wu M, Hu X, Liu J, Liao Y, Deng G-J (2012) Iron-catalyzed 2-arylbenzoxazole formation from o-nitrophenols and benzylic alcohols. Org Lett 14:2722–2725. doi:10.1021/ol300937z
32. Song Q, Feng Q, Zhou M (2013) Copper-catalyzed oxidative decarboxylative arylation of benzothiazoles with phenylacetic acids and α-hydroxyphenylacetic acids with O_2 as the sole oxidant. Org Lett 15:5990–5993. doi:10.1021/ol402871f
33. Zali Boeini H, Hajibabaei Najafabadi K (2009) Efficient one-step synthesis of benzazoles in aqueous media. Eur J Org Chem 2009:4926–4929. doi:10.1002/ejoc.200900740
34. Maybhate SP, Rajamohanan PP, Rajappa S (1991) Regiospecific synthesis of N-sulfonyl derivatives of 3,5-diamino-1*H*-1, 2,4-triazole and 2,5-diamino-1,3,4-thiadiazole. Synthesis 220–222: doi:10.1055/s-1991-26426
35. Franco S, Meléndez E, Merchán FL (1995) Diheterocyclic compounds from dithiocarbamates and derivatives thereof. VII. 1-(2-benzazolylaminophenylsulphonyl)-4-[4-oxo-2-thioxo(oxo)-1,2,3,4-tetrahydro-3-quinazolinyl]benzenes. J Heterocycl Chem 32:1181–1183. doi:10.1002/jhet.5570320414
36. Meléndez E, Merchán FL, Merino P, Orduna J, Urchegui R (1991) Diheterocyclic compounds from dithiocarbamates and derivatives thereof. VI. unsymmetrical N1,N4-Bis(2-benzazolyl)sulphanilamides. J Heterocycl Chem 28:653–656. doi:10.1002/jhet.5570280320
37. Garín J, Meléndez E, Merchán FL, Merino P, Orduna J, Tejero T (1990) Diheterocyclic compounds from dithiocarbamates and derivatives thereof. II. 2,2′-Diamino-6,6′-bibenzoazoles. J Heterocycl Chem 27:321–326. doi:10.1002/jhet.5570270238
38. Rodricks JV, Rapoport H (1971) Synthesis of cyclic guanidines. J Org Chem 36:46–48. doi:10.1021/jo00800a012
39. Chaudhary M, Pareek D, Pareek PK, Kant R, Ojha KG, Pareek A (2011) Synthesis of some new biologically active benzothiazole derivatives containing benzimidazole and imidazoline moieties. Bull Korean Chem Soc 32:131–136. doi:10.5012/bkcs.2011.32.1.131