

## A convenient route for the synthesis of new thiadiazoles

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**Abstract:** The present work describes the preparation of new thiadiazoles through a simple intramolecular reaction of mono- and bis-hydrazoneyl halides with methyl hydrogen phenyl carbonimidodithioate or methyl-2-arylidene hydrazinecarbodithioate. The synthetic method involves nucleophilic substitution followed by intramolecular cyclization reactions mediated by evolution of methanethiol. The structures of the title compounds were elucidated by elemental analyses, and FTIR, MS and NMR spectra.

**Key words:** Hydrazoneyl, thiadiazoles, dithioate

### 1. Introduction

Heterocyclic compounds show interesting biological activities.<sup>1</sup> Thiadiazoles are important in the drug industry because they have antitumor,<sup>2</sup> antihistamine,<sup>3</sup> hypoglycemic,<sup>4</sup> and anticholinergic activity.<sup>5</sup> Thiadiazoles are also biologically active due to the aromaticity of the ring and are used in the treatment of epilepsy.<sup>6,7</sup> They were reported as anti-inflammatory,<sup>8</sup> antimicrobial,<sup>9</sup> and anticonvulsant<sup>10</sup> agents. We previously reported the synthesis of thiadiazoles via reaction of hydrazoneyl halides with carbonothioic dihydrazide or methyl carbodithioate or potassium thiocyanate.<sup>11–13</sup>

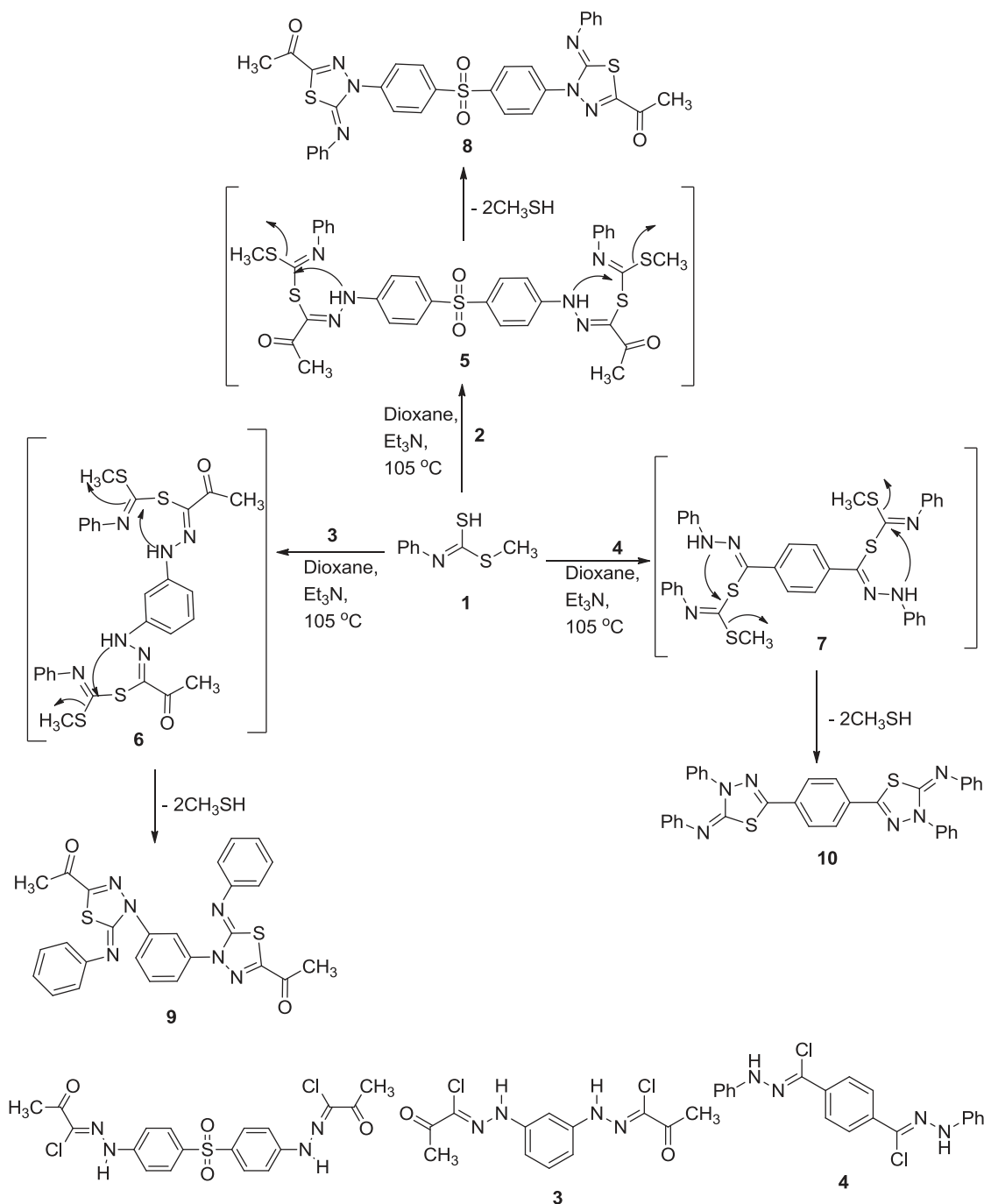
The aim of the present work was the synthesis and characterization of new thiadiazoles based on a simple base-catalyzed cyclization reaction of mono- or bis-hydrazoneyl halides with methyl hydrogen phenyl carbonimidodithioate or methyl-2-arylidene hydrazinecarbodithioate.

### 2. Results and discussion

The nucleophilic substitution reaction of bis-hydrazoneyl dichlorides (**2–4**) with methyl hydrogen phenyl carbonimidodithioate (**1**) in dioxane in the presence of triethylamine under reflux gave the corresponding thiadiazoles products (**8–10**). The reaction of bis-hydrazoneyl dichlorides (**2–4**) with the methyl-N-phenylethanimidodithioate (**1**) afforded the acyclic thiohydrazone (**5–7**) by the attack of hydrazone-NH to iminic C=N followed by elimination of methanethiol to give the final compounds (**8–10**) as depicted in Scheme 1. The mass spectra of the products (**8–10**) revealed in each case a molecular ion peak in agreement with the molecular formula for each product. The IR spectra of the products showed no absorption bands at 3500–3100 cm<sup>-1</sup>, which are characteristic of NH groups. Moreover, the <sup>1</sup>H NMR spectrum for **8–10** indicated the absence of signals attributed

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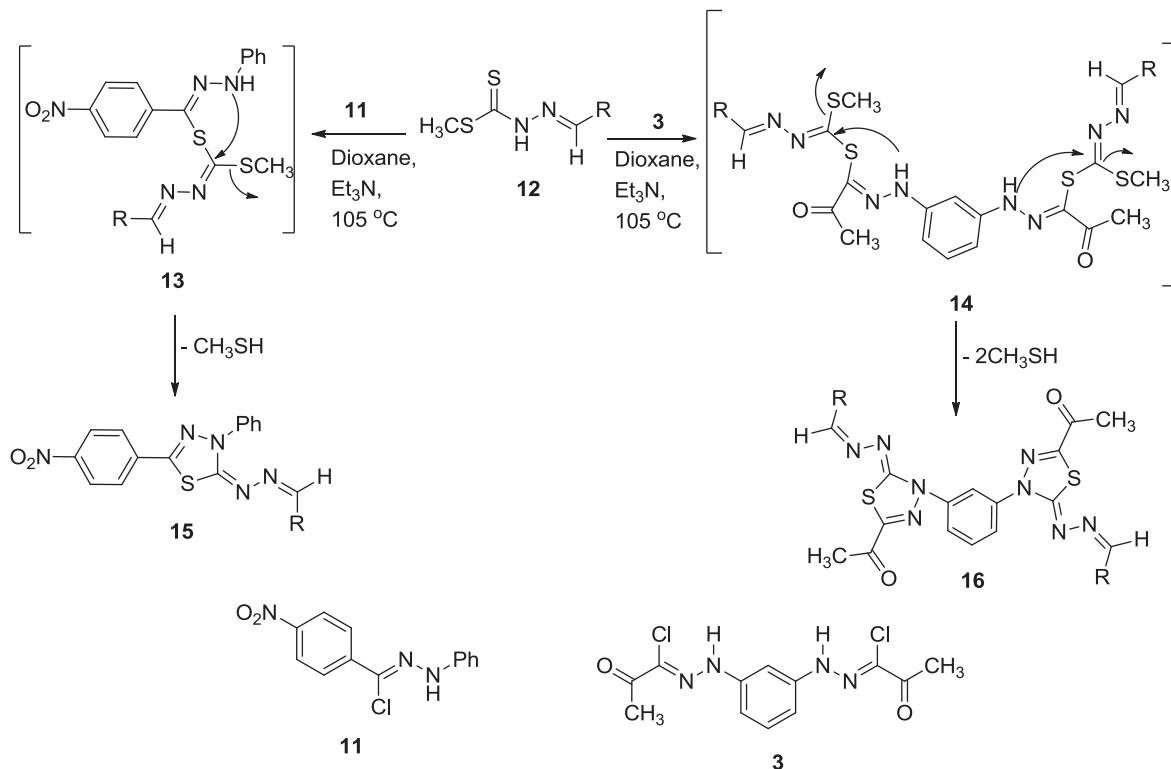
to S-methyl and NH protons. The  $^1\text{H}$  NMR spectrum for compound **10** revealed signals at 7.06–8.26 (m, 24H, ArH) ppm.



**Scheme 1.** Synthesis of thiadiazoles **8**–**10**.

Hydrazonoyl chlorides were used in the synthesis of thiadiazole derivatives.<sup>11</sup> These principles were extended in the present work; thus, methyl-2-arylidene hydrazine-carbodithioate (**12**) was reacted with hydrazonoyl chloride (**3**) or **11** in dioxane and in the presence of triethylamine by heating until complete elimination

of methanethiol gas. The reaction mixture gave a single product in each case (**15** or **16**). The formation of the final products was explained by a nucleophilic substitution reaction to give intermediate **13** or **14**, which was then followed by elimination of methanethiol in order to give the final products (**15** or **16**). The final products were elucidated on the basis of spectral data and elemental analysis (Scheme 2). The IR spectrum of **15** or **16** showed no absorption bands for a NH group around  $3500\text{--}3100\text{ cm}^{-1}$ . Furthermore, the  $^1\text{H}$  NMR spectrum for **15** or **16** showed no signals attributed to NH protons (Scheme 2). The mass spectra of the products revealed in each case a molecular ion peak in agreement with the molecular formula of each compound.



**Scheme 2.** Synthesis of thiadiazoles **15** and **16**.

### 3. Experimental

Melting points were determined on an electrothermal apparatus. IR spectra were recorded using KBr discs on a Shimadzu FT-IR 8201 PC spectrophotometer.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{SO}$  solutions on a Varian Gemini 300 MHz spectrometer and chemical shifts are expressed in  $\delta$  units using TMS as an internal reference. Mass spectra were recorded on a GC-MS QP 1000 EX Shimadzu. Elemental analyses were carried out at the Microanalytical Center of Cairo University.

The starting reagents **1**,<sup>14</sup> **2**,<sup>3</sup> **3**,<sup>13</sup> **4**,<sup>15</sup> **12**,<sup>16</sup> and **11**<sup>17</sup> were prepared as previously described.

#### 3.1. Synthesis of bis-thiadiazoles (8–10)

A mixture of bis-hydrazonoyl dichlorides (**2–4**) (5 mmol) and methyl hydrogen phenylcarbonimidodithioate (**1**) (1.83 g, 10 mmol) was refluxed in dioxane (20 mL) and in the presence of triethylamine (1.1 g, 1.390 mL, 10 mmol) until elimination of all methanethiol gas (8–10 h) and then cooled. The cold reaction mixture was then

poured onto a cold ice–hydrochloric acid mixture with stirring. The solid that precipitated out was collected, washed with water several times, dried, and then recrystallized from DMF/EtOH to give the final products (**8–10**).

**3.1.1. 1,1'-((5,5')-4,4'-(sulfonylbis(4,1-phenylene))bis(5-phenylimino)4,5-dihydro-1,3,4-thiadiazole-4,2-diyl)diethanone (8)**

Brown solid; Yield (70%) mp ? 300 °C. IR (KBr):  $\nu_{max}$  3062 (CH aromatic), 1697 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.49 (s, 6H,  $2 \times \text{CH}_3$ ) and 7.42–7.92 (m, 18H, ArH) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 25.41, 115.18, 125.18, 127.35, 128.89, 131.11, 134.46, 143.41, 146.39, 149.01, 158.01, and 188.42; MS  $m/z$  (%) = 652 ( $\text{M}^+$ , 29); Anal. Calcd for  $\text{C}_{32}\text{H}_{24}\text{N}_6\text{O}_4\text{S}_3$  (652.77): C, 58.88; H, 3.71; N, 12.87; Found: C, 58.89; H, 3.68; N, 12.85%.

**3.1.2. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-(phenylimino-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl)diethanone (9)**

Red brown solid; Yield (55%); mp ? 300 °C. IR (KBr):  $\nu_{max}$  3055 (CH aromatic), 1681 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.51 (s, 6H,  $2 \times \text{CH}_3$ ) and 6.98–7.93 (m, 14H, ArH) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 23.51, 106.81, 118.27, 123.34, 127.41, 130.62, 131.01, 147.01, 146.15, 149.87, 157.32, and 176.59; MS  $m/z$  (%) = 512 ( $\text{M}^+$ , 21); Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{N}_6\text{O}_2\text{S}_2$  (512.11): C, 60.92; H, 3.93; N, 16.39; Found: C, 60.94; H, 3.91; N, 16.35%.

**3.1.3. (N,N'E,N,N'E)-N,N'-(5,5'-(1,4-phenylene)bis(3-phenyl-1,3,4-thiadiazole-5(3H)-yl-2(3H)-ylidene)dianiline (10)**

Brown solid; Yield (51%); mp ? 300 °C. IR (KBr):  $\nu_{max}$  3070 (CH aromatic)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.06–8.26 (m, 24H, ArH) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 108.01, 120.27, 121.84, 123.41, 125.67, 126.83, 129.3, 131.65, 132.09, 133.42, 152.16, and 154.03 ppm; MS  $m/z$  (%) = 580 ( $\text{M}^+$ , 32); Anal. Calcd for  $\text{C}_{34}\text{H}_{24}\text{N}_6\text{S}_2$  (580.72): C, 70.32; H, 4.17; N, 14.47; Found: C, 70.36; H, 4.21; N, 14.41%.

**3.2. General procedure for the preparation of thiadiazoles (15 and 16)**

A mixture of methyl-2-arylidene hydrazine carbodithioates (**12**) (10 mmol) and bis-hydrazoneyl chlorides (**3**) (5 mmol) or hydrazoneyl chloride (**11**) (10 mmol) was refluxed in dioxane (20 mL) and triethylamine (1.01 g, 1.39 mL, 10 mmol) until methanethiol ceased to evolve (6–10 h) and the progress of the reaction was monitored by TLC. The reaction mixture was allowed to cool and then poured into ice–hydrochloric acid with stirring. The solid that precipitated out was collected, washed with water several times, dried, and recrystallized from DMF/MeOH to give the final products (**15** and **16**).

**3.2.1. -2-((4-methoxybenzylidene)hydrazono)-3-(4-methoxyphenyl)-5-(4-nitrophenyl)-2,3-dihydro-1,3,4-thiadiazole (15a)**

Light orange solid; Yield (74%); mp. 188 °C. IR (KBr):  $\nu_{max}$  3051 (CH aromatic), 1626 (C=N) and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 3.89 (s, 3H,  $\text{CH}_3\text{O}$ ) and 7.21–8.39 (m, 14H, ArH and CH=N) ppm; MS  $m/z$  (%) = 431 ( $\text{M}^+$ , 42); Anal. Calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_5\text{O}_3\text{S}_3$  (431.11): C, 61.24; H, 3.97; N, 16.23; Found: C, 61.27; H, 3.94; N, 16.21%.

**3.2.2. -2-((4-methylbenzylidene)hydrazono)-5-(4-nitrophenyl)-3-(p-tolyl)-2,3-dihydro-1,3,4-thiadiazole (15b)**

Light brown solid; Yield (52%); mp 221 °C. IR (KBr):  $\nu_{max}$  3050 (CH aromatic), 1624 (C=N) and 1601 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.39 (s, 3H, CH<sub>3</sub>) and 7.19–8.54 (m, 14H, ArH and CH=N) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 19.21, 121.08, 122.56, 125.46, 128.35, 129.01, 129.62, 129.98, 130.09, 133.02, 134.58, 140.02, 144.61, 146.52, 147.69, 150.61, and 152.27. MS m/z (%) = 415 (M<sup>+</sup>, 29); Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>S (415.10): C, 63.60; H, 4.12; N, 16.86; Found: C, 63.59; H, 4.15; N, 16.89%.

**3.2.3. 2-(-2-((2-hydroxybenzylidene)hydrazono)-5-(4-nitrophenyl)-1,3,4-thiadiazol-3(2H)-yl)phenol (15c)**

Red solid; Yield (49%); mp 198 °C. IR (KBr):  $\nu_{max}$  3327 (OH), 3035 (CH aromatic), 1612 (C=N) and 1604 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.09–8.29 (m, 14H, ArH and CH=N) and 10.44 (s, 1H, OH) ppm; MS m/z (%) = 417 (M<sup>+</sup>, 51); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>5</sub>O<sub>3</sub>S (417.44): C, 60.42; H, 3.62; N, 16.78; Found: C, 60.44; H, 3.59; N, 16.79%.

**3.2.4. -2-(benzylidenehydrazono)-5-(4-nitrophenyl)-3-phenyl-2,3-dihydro-1,3,4-thiadiazole (15d)**

Orange solid; Yield (45%); mp 211 °C. IR (KBr):  $\nu_{max}$  3059 (CH aromatic), 1629 (C=N) and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.33–8.36 (m, 15H, ArH and CH=N) ppm; MS m/z (%) = 401 (M<sup>+</sup>, 37); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>S (401.1): C, 62.83; H, 3.77; N, 17.45; Found: C, 62.85; H, 3.79; N, 17.41%.

**3.2.5. -2-(-4-chlorobenzylidene)hydrazono)-3-(4-chlorophenyl)-5-(4-nitrophenyl)-2,3-dihydro-1,3,4-thiadiazole (15e)**

Orange solid; Yield (61%); mp 201 °C. IR (KBr):  $\nu_{max}$  3051 (CH aromatic), 1628 (C=N) and 1604 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.09–8.41 (m, 14H, ArH and CH=N) ppm; MS m/z (%) = 435 (M<sup>+</sup>, 39); Anal. Calcd for C<sub>21</sub>H<sub>14</sub>ClN<sub>5</sub>O<sub>2</sub>S (435.89): C, 57.86; H, 3.24; N, 16.07; Found: C, 57.89; H, 3.26; N, 16.01%.

**3.2.6. -2-(-4-bromobenzylidene)hydrazono)-3-(4-bromophenyl)-5-(4-nitrophenyl)-2,3-dihydro-1,3,4-thiadiazole (15f)**

Brown solid; Yield (58%); mp 213 °C. IR (KBr):  $\nu_{max}$  3042 (CH aromatic), 1620 (C=N) and 1599 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.11–7.54 (m, 14H, ArH and CH=N) ppm; MS m/z (%) = 480 (M<sup>+</sup>, 26); Anal. Calcd for C<sub>21</sub>H<sub>14</sub>BrN<sub>5</sub>O<sub>2</sub>S (480.34): C, 52.51; H, 2.94; N, 14.58; Found: C, 52.49; H, 2.95; N, 14.55%.

**3.2.7. -2-((4-nitrobenzylidene)hydrazono)-3,5-bis(4-nitrophenyl)-2,3-dihydro-1,3,4-thiadiazole (15g)**

Brown solid; Yield (63%); mp 227 °C. IR (KBr):  $\nu_{max}$  3050 (CH aromatic), 1629 (C=N) and 1601 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 7.31–8.56 (m, 14H, ArH and CH=N) ppm; MS m/z (%) = 446 (M<sup>+</sup>, 62); Anal. Calcd for C<sub>21</sub>H<sub>14</sub>N<sub>6</sub>O<sub>4</sub>S (446.44): C, 56.50; H, 3.16; N, 18.82; Found: C, 56.51; H, 3.19; N, 18.86%.

**3.2.8. 3-(furan-2-yl)-2-((furan-2-ylmethylene)hydrazono)-5-(4-nitrophenyl)-2,3-dihydro-1,3,4-thiadiazole (15h)**

Brown solid; Yield (69%); mp 202 °C. IR (KBr):  $\nu_{max}$  3060 (CH aromatic), 1632(C=N) and 1601 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 6.51–7.89 (m, 12H, ArH and Furan H's) 8.21 (s, 2H, CH=N) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 113.05, 117.82, 124.03, 125.36, 126.21, 128.09, 129.54, 130.94, 134.76, 138.32, 140.75, 144.39, 148.02, 150.36, 156.82, and 159.79. MS m/z (%) = 391 ( $\text{M}^+$ , 18); Anal. Calcd for  $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}_3\text{S}$  (391.40): C, 58.30; H, 3.35; N, 17.89; Found: C, 58.33; H, 3.36; N, 17.87%.

**3.2.9. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((4-methoxybenzylidene) hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16a)**

Brown solid; Yield (79%); mp 258 °C. IR(KBr):  $\nu_{max}$  3085 (CH aromatic), 1658 (C=O), 1623 (C=N), and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.34 (s, 6H, 2CH<sub>3</sub>); 3.88 (s, 6H, 2CH<sub>3</sub>O) and 6.99–8.14 (m, 14H, ArH and CH=N) ppm; MS m/z (%) = 626 ( $\text{M}^+$ , 51); Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_4\text{S}_2$  (626.15): C, 57.49; H, 4.18; N, 17.88; Found: C, 57.46; H, 4.19; N, 17.92%.

**3.2.10. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((4-methylbenzylidene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16b)**

Brown solid; Yield (63%); mp 304 °C. IR (KBr):  $\nu_{max}$  3054 (CH aromatic), 1667 (C=O), 1615 (C=N), and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.49 (s, 6H, 2CH<sub>3</sub>) and 7.01–8.24 (m, 20H, ArH and CH=N) ppm; MS m/z (%) = 594 ( $\text{M}^+$ , 38); Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{N}_8\text{O}_2\text{S}_2$  (594.16): C, 60.59; H, 4.41; N, 18.84; Found: C, 60.62; H, 4.45; N, 18.88%.

**3.2.11. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-(-(2-hydroxybenzylidene) hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16c)**

Brown solid; Yield (38%); mp 258 °C. IR (KBr):  $\nu_{max}$  3317 (OH), 3085 (CH aromatic), 1666 (C=O), 1615 (C=N), and 1604 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.51 (s, 6H, 2CH<sub>3</sub>), 7.06–8.25 (m, 14H, ArH and CH=N) and 10.39 (s, 2H, OH) ppm; MS m/z (%) = 598 ( $\text{M}^+$ , 58); Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_4\text{S}_2$  (598.12): C, 56.18; H, 3.70; N, 18.72; Found: C, 56.21; H, 3.69; N, 18.74%.

**3.2.12. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-(-(benzylidene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16d)**

Brown solid; Yield (48%); mp 267 °C. IR (KBr):  $\nu_{max}$  3055 (CH aromatic), 1658 (C=O), 1613 (C=N), and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.52 (s, 6H, 2CH<sub>3</sub>) and 7.12–8.24 (m, 16H, ArH and CH=N) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ ): 21.67, 109.37, 122.87, 125.39, 127.58, 129.84, 130.98, 131.97, 139.56, 146.47, 1498.03, 159.37, and 188.07. MS m/z (%) = 566 ( $\text{M}^+$ , 49); Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_2\text{S}_2$  (566.13): C, 59.35; H, 3.91; N, 19.77; Found: C, 59.35; H, 3.92; N, 19.74%.

**3.2.13. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((4-chlorobenzylidene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16e)**

Brown solid; Yield (74%); mp. 263 °C. IR (KBr):  $\nu_{max}$  3109 (CH aromatic), 1665 (C=O), 1612 (C=N), and 1599 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.51 (s, 6H, 2CH<sub>3</sub>) and 7.14–8.33 (m, 14H, ArH and CH=N) ppm; MS  $m/z$  (%) = 635 (M<sup>+</sup>, 61); Anal. Calcd for C<sub>28</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (635.55): C, 52.92; H, 3.17; N, 17.63; Found: C, 52.93; H, 3.19; N, 17.65%.

**3.2.14. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((4-bromobenzylidene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16f)**

Yellow Brown solid; Yield (18%); mp 259 °C. IR (KBr):  $\nu_{max}$  3086 (CH aromatic), 1659 (C=O), 1627 (C=N), and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.50 (s, 6H, 2CH<sub>3</sub>) and 7.18–8.44 (m, 14H, ArH and CH=N) ppm; MS  $m/z$  (%) = 724 (M<sup>+</sup>, 38); Anal. Calcd for C<sub>28</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (724.95): C, 46.42; H, 2.78; N, 15.47; Found: C, 46.42; H, 2.75; N, 15.48%.

**3.2.15. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((4-nitrobenzylidene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16g)**

Deep brown solid; Yield (71%); mp ? 300 °C. IR (KBr):  $\nu_{max}$  3078 (CH aromatic), 1666 (C=O), 1623 (C=N), and 1579 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.53 (s, 6H, 2CH<sub>3</sub>) and 7.22–8.42 (m, 14H, ArH and CH=N) ppm; MS  $m/z$  (%) = 656 (M<sup>+</sup>, 54); Anal. Calcd for C<sub>28</sub>H<sub>20</sub>N<sub>10</sub>O<sub>6</sub>S<sub>2</sub> (656.1): C, 51.21; H, 3.07; N, 21.33; Found: C, 51.23; H, 3.08; N, 21.37%.

**3.2.16. 1,1'-((5,5')-4,4'-(1,3-phenylene)bis(5-((furan-2-ylmethylene)hydrazono)-4,5-dihydro-1,3,4-thiadiazole-4,2-diyl))diethanone (16h)**

Deep brown solid; Yield (56%); mp ? 300 °C. IR (KBr):  $\nu_{max}$  3117 (CH aromatic), 1666 (C=O), 1629 (C=N), and 1605 (C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO- $d_6$ ): 2.49 (s, 6H, 2CH<sub>3</sub>) and 6.99–8.36 (m, 12H, ArH, Furan H's and CH=N) ppm; MS  $m/z$  (%) = 546 (M<sup>+</sup>, 47); Anal. Calcd for C<sub>24</sub>H<sub>18</sub>N<sub>8</sub>O<sub>4</sub>S<sub>2</sub> (546.09): C, 52.74; H, 3.32; N, 20.50; Found: C, 52.71; H, 3.36; N, 20.49%.

**4. Conclusions**

We reported the synthesis and characterization of new thiadiazoles based on a simple base-catalyzed cyclization reaction of mono- or bis-hydrazonoyl halides with methyl hydrogen phenyl carbonimidodithioate or methyl-2-arylidene hydrazinecarbodithioate.

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## References

1. Shawali, A. S. *J. Adv. Res.* **2014**, *5*, 1–17.
2. Padwa, A. *Angew. Chem. Int. Ed.* **1976**, *15*, 123–136.
3. Abdelhamid A. O.; Attaby, F. A. *J. Heterocycl. Chem.* **1991**, *28*, 41–44.
4. Huisgen, R.; Sustmann, R.; Wallbillich, G. *Chem. Ber.* **1967**, *100*, 1786–1801.
5. Kornis, G. I. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R.; Ress, C. W.; Scriven, E. F. V., Eds.; Pergamon Press: London, UK, 1996; Vol. 4, pp 379.
6. Malawska, B. *Curr. Top. Med. Chem.* **2005**, *5*, 69–85.
7. Barboiu, M.; Cimpoesu, M.; Guran, C.; Supuran, C. T. *Met.-Based Drugs* **1996**, *3*, 227–232.
8. Labanauskas, L.; Kalcas, V.; Udrenaitė, E.; Gaidelis, P.; Brukstus, A.; Dauksas, V. *Pharmazie* **2001**, *56*, 617–619.
9. Dogan, H. N.; Duran, A.; Rollas, S.; Sener, G.; Uysal, M. K.; Gulen, D. *Bioorg. Med. Chem.* **2002**, *10*, 2893–2898.
10. Ilies, M. A.; Masereel, B.; Rolin, S.; Scozzafava, A.; Campeanu, G.; Campeanu, V.; Supuran, C. T. *Bioorg. Med. Chem.* **2004**, *12*, 2717–2726.
11. Sayed, A. R. *Tetrahedron Lett.* **2010**, *51*, 4490–4493.
12. Abdelhamid, A. O.; Sayed, A. R.; Zaki, Y. H. *Phosphorus Sulfur Silicon Relat. Elem.* **2007**, *182*, 1447–1457.
13. Sayed, A. R.; Gomha, S. M.; Farghaly, T. A. *J. Heterocycl. Chem.* **2015**, in press DOI 10.1002/jhet.2320.
14. Servi, S.; Genc, M.; Gür, S.; Koca, M. *Eur. J. Med. Chem.* **2005**, *40*, 687–693.
15. Stille, J. K.; Harris, F. W. *J. Polymer Sci. B Polymer Lett.* **1966**, *4*, 333–336.
16. Badawy, M. A.; Abdelhady, S. A.; Ibrahim Y. A. *Liebigs Ann. Chem.* **1990**, 393–395.
17. Trishin, Yu. G. *Russ. Chem. Bull.* **2005**, *54*, 1637–1641.