

## Chemoselective Synthesis of Novel Thiatriazolophanes

*Madhukar S. Chande,\* Kiran A. Puthamane, Pravin A. Barve, Rahul R. Khanwelkar and Deepak S. Venkataraman*

*Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai 400 032, India*

Bis-[4-alkyl/aryl-5-thia-1,2,4-triazóis] foram preparados pela fusão de diácidos e tiosemicarbazidas, pela condensação de hidrazidas ácidas aromáticas com isotiocianato. A alquilação quimiosseletiva destes bis-[4-alkyl/aryl-5-thia-1,2,4-triazóis] com 1,ω-dihaloalcanos na presença de hidróxido de potássio em metanol aquoso, proporcionou N-alkyl/aryl thiatriazolofanos inéditos.

Bis-[4-alkyl/aryl-5-thia-1,2,4-triazoles] were prepared by fusion of diacids and thiosemicarbazides by condensation of aromatic acid hydrazides with isothiocyanate. Chemoselective alkylation of these bis-[4-alkyl/aryl-5-thia-1,2,4-triazoles] with 1,ω-dihaloalkanes in presence of potassium hydroxide in aqueous methanol afforded novel N-alkyl/aryl thiatriazolophanes.

**Keywords:** 4-alkyl/aryl-5-thia-1,2,4-triazoles, 1,ω-dihaloalkanes, N-alkyl/aryl thiatriazolophanes, chemoselectivity

### Introduction

Crown compounds have generated considerable interest during the last three decades because of their ability to form stable complexes with a variety of metal and organic cations and anions.<sup>1</sup> They also have wide applications in phase transfer catalysis.<sup>2</sup> In recent years various structural changes have been made to the basic “crown ether” structure in order to enhance the selective activity of the ligands.<sup>3</sup> These changes involve the insertion of aromatic and/or heterocyclic ring systems into the macrocycles. Incorporation of heterocyclic subunit provides rigidity to the macrocycle and contributes in increasing the stability of complexes formed with both metals and organic cations.<sup>3</sup> The development of crown compounds especially macrocyclic compounds containing heterocyclic subunit has gained importance due to their wide range of applications. Several reviews and monographs have been published which highlight their synthesis and application in synthetic organic chemistry as phase transfer catalysts and in analytical chemistry as ligand for complexation.<sup>2,4</sup>

In recent years, attention has been increasingly paid to the synthesis of bisheterocyclic compounds, which exhibit various biological activities.<sup>5</sup> including antibacterial, antifungal, tuberculostatic and plant growth regulative properties. Bisheterocyclic compounds displayed much better antibacterial activity than heterocyclic compounds.<sup>6</sup> Various 1,2,4-triazoles are found to be associated with diverse pharmacological activities such as antiasthmatic,<sup>7</sup> antiviral (ribavirin),<sup>8</sup> antifungal (fluconazole),<sup>9</sup> antimicrobial,<sup>10</sup> antibacterial,<sup>11</sup> insecticidal,<sup>11,12</sup> amoebicidal,<sup>13</sup> hypnotic,<sup>14</sup> cytotoxic,<sup>15</sup> and hypotensive<sup>16</sup> activities. This moiety was also found in potent agonist and antagonist receptor ligands,<sup>17</sup> in HIV-1 protease inhibitors<sup>18</sup> and in thrombin inhibitors.<sup>19</sup> Along with these significant pharmaceutical uses, 1,2,4-triazole derivatives are effectively used in polymers, dyestuff, photographic chemicals and agricultural chemicals.<sup>20</sup>

We have previously reported the chemoselective synthesis of novel oxadiazolophanes<sup>21</sup> and N-aminotriazolophanes.<sup>22</sup> In continuation of this ongoing program in the synthesis of novel macrocyclic ligands<sup>21,22</sup> their computational studies<sup>21,22</sup> and their application as phase transfer catalyst (PTC),<sup>22</sup> we now report a facile chemoselective synthesis of novel N-alkyl/aryl thiatriazolophanes.

\*e-mail: mschande@yahoo.com

## Results and Discussion

The present work describes a versatile synthetic strategy for the chemoselective synthesis of novel N-alkyl/aryl thiatriazolophanes. Obtained heterophanes would be similar to lariat ether<sup>23</sup> with N-alkyl/aryl groups as side arm. The study of the stereochemistry of these compounds is of interest as the two N-alkyl/aryl groups would be either *cis* or *trans* to each other depending on the alkyl chain joining the two heterocyclic units and the thermodynamic stability of the molecule.

There are many methods described in the literature for the synthesis of N-substituted-1,2,4-triazoles,<sup>20</sup> but none of them concerns the synthesis of heterophanes. Bis N-alkyl/aryl thiatriazoles **3a-c** were prepared in good yield by direct fusion of adipic acid **1** with thiosemicarbazides **2a-c**, according to Xu method<sup>24</sup> (Scheme 1). This compound **3** containing thioamido groups has an amphoteric nature and can exist in tautomeric forms 3A and 3B. On alkylation of **3** with 1, $\omega$ -dihaloalkane, multiple products could form depending on the reactions conditions.

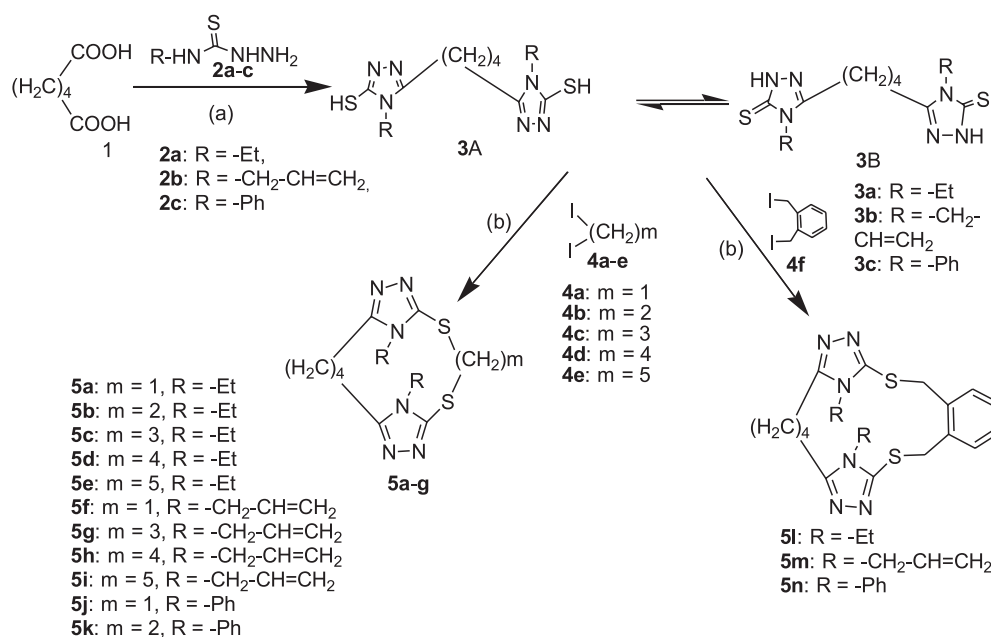
Reaction of compounds **3a-c** with diiodoalkanes **4a-f** in aq. methanol (80%) in the presence of potassium hydroxide as a base gave only products **5a-n** chemoselectively in good yield (Scheme 1, Table 1). The reaction was carried out in large excess of solvent to ensure intramolecular cyclisation (high dilution condition).

The elucidation of structures **5a-n** was accomplished on the basis of their spectral data and elemental analysis (Table 1). For example, reaction of **3a** with 1,2 diiodoethane **4b** resulted in the formation of the desired

N-ethylthiatriazolophane **5b**, confirmed on the basis of NMR spectra. <sup>1</sup>H NMR spectrum of the compound showed triplet at  $\delta$  4.10 for S-CH<sub>2</sub> group of ethane chain. Absence of peak for C=S in <sup>13</sup>C NMR spectrum confirmed the chemoselectivity of S-alkylation. It showed signal for S-CH<sub>2</sub> carbon at 32.1 ppm. From the above data compound **5c** was identified as 1<sup>4</sup>,6<sup>4</sup>-diethyl-7,11-dithia-1,6(3,5)-di-(1,2,4-triazola)cycloundecaphane.<sup>25</sup> The other thiatriazolophanes **5a-n** were similarly synthesized and characterized.

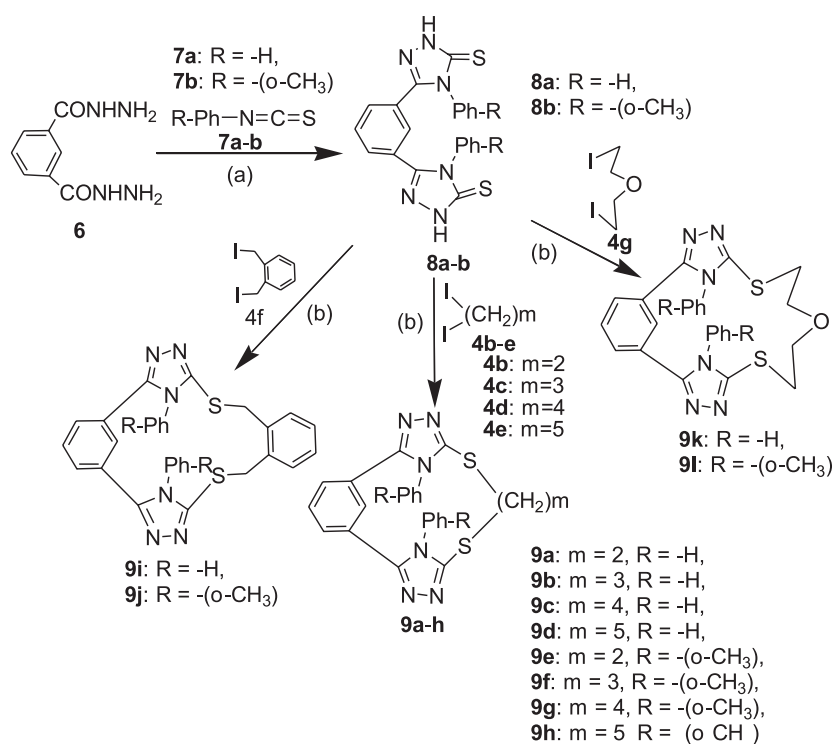
In order to improve the solubility of the thiatriazolophanes, it was thought to incorporate a phenyl nucleus into the structure, which would also help in complexation by PTC. Hence, the scope of the previous reaction was extended to the synthesis of benzotriazolophanes **9** (Scheme 2). Bistriazoles **8** was synthesized in high yield, by reacting isophthalic acid dihydrazide **6** with phenyl/*o*-tolyl isothiocyanates **7**.

The reaction of **8a-b** with **4a-g** in aqueous methanol (80%) in the presence of potassium hydroxide as a base gave desired benzotriazolophanes **9a-l** chemoselectively in moderate yield (Scheme 2, Table 1). Structures of the products were confirmed on the basis of spectral data and elemental analysis (Table 1). For example, reaction of **8a** with 1,2-diiodoethane **4b** resulted in the formation of desired benzotriazolophane **9a**, confirmed on the basis of NMR spectra. <sup>1</sup>H NMR spectrum of the compound showed triplet at  $\delta$  3.46 for S-CH<sub>2</sub> group of ethane chain. Absence of peak for C=S in <sup>13</sup>C NMR spectrum confirmed the chemoselectivity of S-alkylation. It showed signals for S-CH<sub>2</sub> carbons at 31.8 ppm.



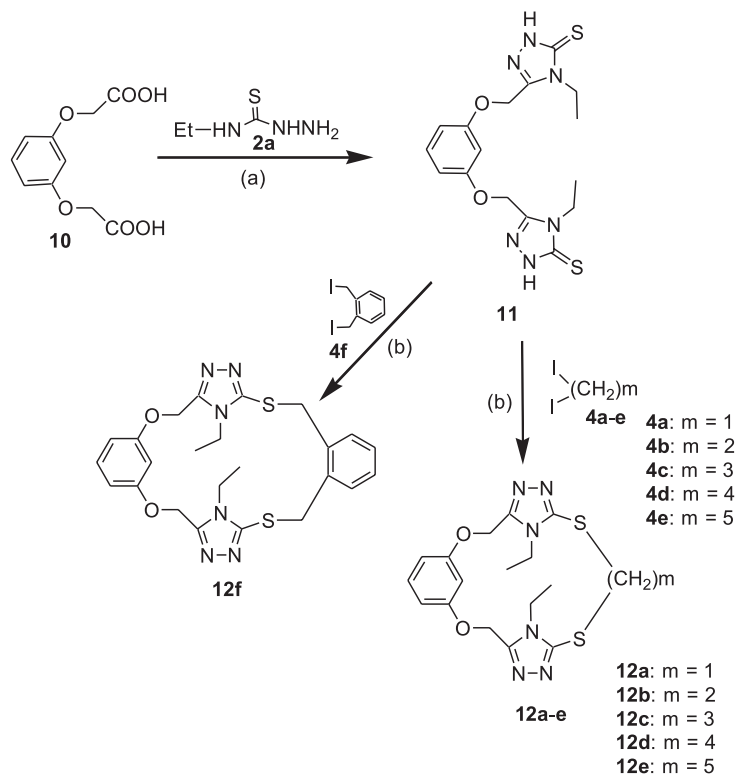
Reagents and conditions: (a) 140 °C, fusion; (b) KOH, aq. MeOH (80%), 80 °C.

**Scheme 1.** Synthesis of N-alkyl/aryl thiatriazolophanes **5**.



Reagents and conditions: (a) i) methanol, 75 °C, ii) KOH, 140 °C, heating; (b) KOH, aq. MeOH (80%), 80 °C.

**Scheme 2.** Synthesis of benzotriazolophanes **9**.

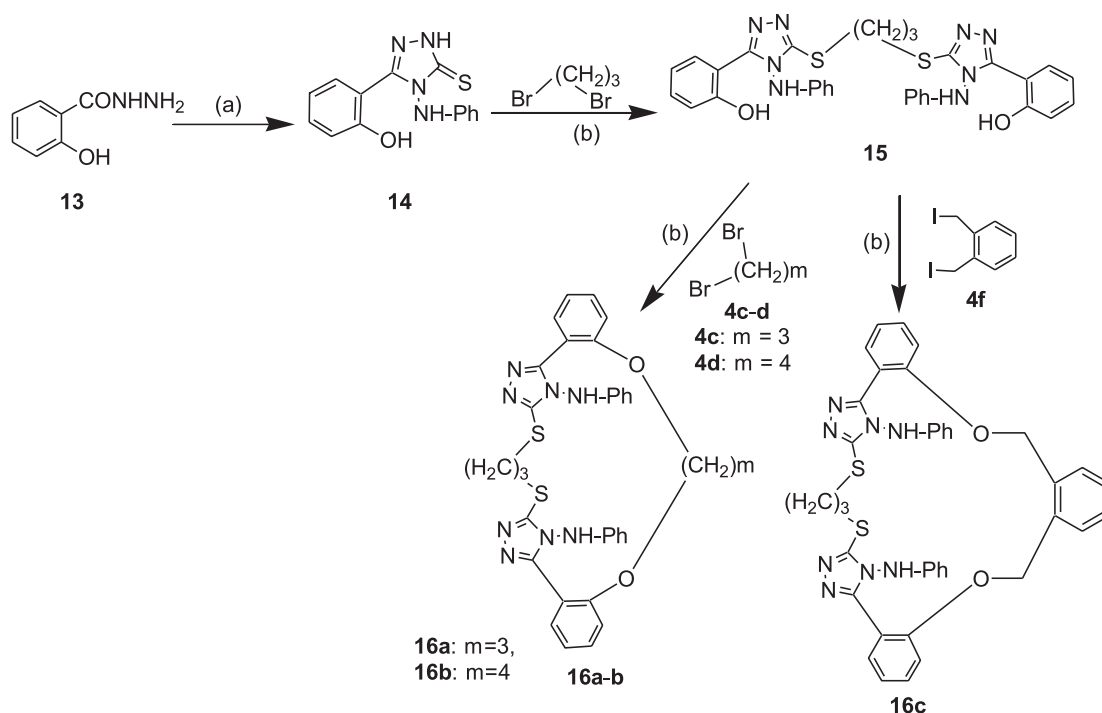


Reagents and conditions: (a) 140 °C, fusion; (b) KOH, aq. MeOH (80%), 80 °C.

**Scheme 3.** Synthesis of N-ethylthiazotriazolophanes **12**.

**Table 1.** Preparation and analytical data of compounds

Compound	Yield / %	mp / °C	Formulae	Required (Found) / %			
				C	H	N	S
<b>3a</b>	80	250	C <sub>12</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	46.10 (46.00)	6.41 (6.26)	26.90 (26.80)	20.50 (20.37)
<b>3b</b>	77	285	C <sub>14</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	50.00 (49.86)	5.95 (5.84)	25.00 (24.90)	19.00 (18.89)
<b>3c</b>	72	>300	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> S <sub>2</sub>	58.82 (58.66)	4.90 (4.80)	20.58 (20.46)	15.68 (15.56)
<b>5a</b>	48	272	C <sub>13</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	48.12 (47.99)	6.21 (6.07)	25.90 (25.78)	19.76 (19.68)
<b>5b</b>	49	265	C <sub>14</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub>	49.68 (46.59)	6.55 (6.41)	24.83 (24.69)	18.95 (18.81)
<b>5c</b>	39	Semisolid	C <sub>15</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub>	51.11 (50.98)	6.86 (6.75)	23.84 (23.74)	18.19 (18.06)
<b>5d</b>	43	125	C <sub>16</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	52.43 (52.29)	7.15 (7.04)	22.93 (22.81)	17.50 (17.36)
<b>5e</b>	41	87	C <sub>17</sub> H <sub>28</sub> N <sub>6</sub> S <sub>2</sub>	53.65 (53.52)	7.42 (7.31)	22.08 (22.00)	16.85 (16.75)
<b>5f</b>	35	185	C <sub>20</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	51.70 (51.58)	5.78 (5.68)	24.12 (24.02)	18.40 (18.25)
<b>5g</b>	45	240	C <sub>15</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	54.23 (54.08)	6.42 (6.31)	22.32 (22.23)	17.03 (16.91)
<b>5h</b>	37	Semisolid	C <sub>17</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub>	55.35 (55.21)	6.71 (6.57)	21.52 (21.41)	16.42 (16.29)
<b>5i</b>	38	Semisolid	C <sub>18</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	56.40 (56.31)	6.98 (6.86)	20.77 (20.67)	15.85 (15.71)
<b>5j</b>	35	Semisolid	C <sub>19</sub> H <sub>28</sub> N <sub>6</sub> S <sub>2</sub>	59.97 (59.91)	4.79 (4.68)	19.98 (19.92)	15.25 (15.16)
<b>5k</b>	43	105	C <sub>22</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	60.80 (60.71)	5.10 (4.99)	19.34 (19.29)	14.76 (14.66)
<b>5l</b>	37	>300	C <sub>21</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	52.43 (52.29)	7.15 (7.04)	22.93 (22.81)	17.50 (17.36)
<b>5m</b>	42	>300	C <sub>22</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub>	60.24 (60.18)	5.93 (5.89)	19.17 (19.06)	14.61 (14.54)
<b>5n</b>	41	175	C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	65.85 (65.78)	5.13 (5.02)	16.46 (16.39)	12.56 (12.45)
<b>8a</b>	77	295	C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub>	61.70 (61.58)	3.69 (3.55)	19.68 (19.56)	14.93 (14.82)
<b>8b</b>	73	285	C <sub>24</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	63.10 (63.00)	4.45 (4.34)	18.39 (18.27)	14.06 (13.98)
<b>9a</b>	43	162	C <sub>24</sub> H <sub>18</sub> N <sub>6</sub> S <sub>2</sub>	63.40 (63.29)	3.99 (3.85)	18.56 (18.44)	14.05 (13.91)
<b>9b</b>	42	286	C <sub>25</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub>	64.08 (64.00)	4.29 (4.19)	18.01 (17.90)	13.62 (13.50)
<b>9c</b>	45	154	C <sub>26</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub>	64.69 (64.54)	4.60 (4.50)	17.38 (17.30)	13.33 (13.24)
<b>9d</b>	48	270	C <sub>27</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub>	65.29 (65.20)	4.78 (4.70)	17.02 (16.88)	12.91 (12.80)
<b>9e</b>	40	152	C <sub>26</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub>	64.69 (64.55)	4.60 (4.48)	17.45 (17.34)	13.26 (13.14)
<b>9f</b>	45	135	C <sub>27</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub>	65.29 (65.18)	4.86 (4.74)	16.96 (16.87)	12.87 (12.77)
<b>9g</b>	40	140	C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	65.91 (65.80)	5.08 (5.00)	16.45 (16.33)	12.56 (12.45)
<b>9h</b>	45	>300	C <sub>29</sub> H <sub>28</sub> N <sub>6</sub> S <sub>2</sub>	66.38 (66.30)	5.36 (5.28)	15.98 (15.88)	12.27 (12.15)
<b>9i</b>	45	280	C <sub>30</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub>	67.90 (67.77)	4.16 (4.09)	15.88 (15.75)	12.06 (11.98)
<b>9j</b>	57	285	C <sub>32</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub>	68.80 (68.70)	4.70 (4.66)	15.11 (15.00)	11.39 (11.28)
<b>9k</b>	42	120	C <sub>26</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O	62.68 (62.55)	4.40 (4.28)	16.90 (16.77)	12.81 (12.70)
<b>9l</b>	59	105	C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub> O	63.85 (63.78)	4.98 (4.86)	16.02 (15.95)	12.11 (12.00)
<b>11</b>	85	184	C <sub>16</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	48.96 (48.86)	5.14 (5.00)	21.41 (21.30)	16.34 (16.20)
<b>12a</b>	37	119	C <sub>17</sub> H <sub>20</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	50.48 (50.33)	4.98 (4.84)	20.78 (20.66)	15.85 (15.72)
<b>12b</b>	38	195	C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	51.65 (51.50)	5.30 (5.15)	20.08 (20.00)	15.32 (15.22)
<b>12c</b>	38	188	C <sub>19</sub> H <sub>24</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	52.76 (52.60)	5.59 (5.44)	19.43 (19.31)	14.48 (14.39)
<b>12d</b>	35	160	C <sub>20</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	53.79 (53.64)	5.87 (5.72)	18.82 (18.72)	14.36 (14.23)
<b>12e</b>	37	142	C <sub>21</sub> H <sub>28</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub>	54.76 (54.61)	6.13 (6.00)	18.25 (18.13)	13.92 (13.79)
<b>12f</b>	36	133	C <sub>24</sub> H <sub>26</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	58.28 (58.12)	5.30 (5.15)	16.99 (16.88)	12.97 (12.83)
<b>14</b>	75	224	C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> SO	59.14 (59.01)	4.25 (4.09)	19.70 (19.57)	11.28 (11.13)
<b>15</b>	63	182	C <sub>31</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> O <sub>2</sub>	61.16 (61.07)	4.64 (4.50)	18.41 (18.33)	10.54 (10.42)
<b>16a</b>	30	168	C <sub>34</sub> H <sub>32</sub> N <sub>8</sub> S <sub>2</sub> O <sub>2</sub>	62.94 (62.82)	4.97 (4.83)	17.27 (17.15)	9.88 (9.79)
<b>16b</b>	39	159	C <sub>35</sub> H <sub>34</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub>	63.42 (63.31)	5.17 (5.05)	16.91 (16.78)	9.68 (9.55)
<b>16c</b>	37	142	C <sub>39</sub> H <sub>34</sub> N <sub>8</sub> S <sub>2</sub> O <sub>2</sub>	65.81 (65.68)	4.82 (4.69)	15.76 (15.65)	9.02 (8.90)



Reagents and conditions: (a) (i)  $\text{CS}_2$ , KOH, MeOH, 0–5 °C, (ii)  $\text{PhNHNH}_2$ , fusion, 140 °C; (b) KOH, aq. MeOH (80%), 80 °C.

**Scheme 4.** Synthesis of benzotriazolophanes **16**.

To further explore the chelating properties of benzotriazolophanes, it was decided to incorporate “-O-” linkage in the heterophane skeleton. Hence, in continuation to this work on benzotriazolophanes, 3-carboxymethoxy phenoxyacetic acid **10** was fused with 4-ethyl thiosemicarbazide **2a** to give compound **11** in high yield (Scheme 3). When **11** was reacted with 1,3-diiodopropane **4c** in methanolic potassium hydroxide, compound **12c** was afforded chemoselectively in moderate yield (Scheme 3, Table 1). Structure of the product was confirmed on the basis of spectral data and elemental analysis (Table 1).  $^1\text{H}$  NMR spectrum of the compound showed triplet at  $\delta$  3.62 for  $\text{S-CH}_2$  group of propane chain and quintet at  $\delta$  3.02 for the central propyl  $\text{-CH}_2$ . The other thiatriazolophanes **12a-f** were similarly synthesized and characterized.

We have discussed in detail the chemoselective N-alkylation<sup>22</sup> and S-alkylation<sup>21,22</sup> for the synthesis of triazolophanes. In continuation to our work on O-alkylation for the synthesis of heterophanes with amino side arms,<sup>22</sup> we now report the synthesis of novel N-substituted benzotriazolophanes. Salicylic acid hydrazide **13** was reacted with phenyl hydrazine, carbon disulphide and potassium hydroxide in methanol to give compound **14** in high yield (Scheme 4). When **14** was reacted with 1,3-diiodopropane in methanolic potassium hydroxide, compound **15** was afforded chemoselectively

in good yield (Scheme 4, Table 1). Benzotriazolophanes **16a-c** were subsequently synthesized in moderate yield by reacting **15** with diiodoalkanes in aqueous methanol (80%) containing potassium hydroxide (Scheme 4, Table 1). Structures of the products were confirmed on the basis of spectral data and elemental analysis (Table 1). For example, reaction of **15** with 1,3-diiodopropane resulted in the formation of the desired compound **16a**, which was confirmed on the basis of NMR spectra.  $^1\text{H}$  NMR spectrum of the compound showed triplet at  $\delta$  3.62 for  $\text{-SCH}_2$  group of propane chain and triplet at  $\delta$  4.18 for the propyl  $\text{-OCH}_2$  groups.  $\text{M}^+$  peak at  $m/z$  648 in mass spectrum confirmed the formation of **16a**.

## Conclusion

In this paper, we have reported a versatile and convenient route for the synthesis of novel N-alkyl/aryl thiatriazolophanes from aliphatic and aromatic acids.

## Experimental

The NMR spectra were recorded on Bruker AMX 500 spectrometer at 25 °C. Melting points were taken in open capillaries and are uncorrected. Mass spectra were recorded on Shimadzu GC-MS instrument.

*General procedure for the synthesis of bis-(4-alkyl/aryl-5-mercapto-1,2,4-triazol-3-yl)butane (3a-c)*

0.01 mol of adipic acid and 0.02 mol of alkyl/aryl thiosemicarbazide were mixed together using mortar and pestle. This mixture was fused on oil-bath at 140 °C for 4h, and then cooled to room temperature and the obtained solid mass was dumped into ice-cold water. Brown colored mass was separated by filtration and washed thoroughly with water. Then it dissolved in aqueous 10% sodium hydroxide solution and the insoluble impurities were removed by filtration. The filtrate was then acidified using aqueous 1 mol L<sup>-1</sup> HCl till the pH of the solution became 2. Separated white colored product was filtered, washed with water and dried under vacuum.

*Bis-(4-ethyl-5-mercapto-1,2,4-triazol-3-yl)butane (3a)*

<sup>1</sup>H NMR, (DMSO d<sub>6</sub>): δ 13.51 (s, 2H, 2NH, D<sub>2</sub>O exchangeable), 3.92 (q, 4H, 2NCH<sub>2</sub>), 2.70 (t, 4H, 2CH<sub>2</sub>), 1.91 (p, 4H, 2CH<sub>2</sub>), 1.16 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 165.0 (2C=S), 155.4 (2C=N), 39.2 (2NCH<sub>2</sub>), 25.9 (2CH<sub>2</sub>), 24.0 (2CH<sub>2</sub>), 15.7 (2CH<sub>3</sub>).

*Bis-(4-allyl-5-mercapto-1,2,4-triazol-3-yl)butane (3b)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 13.60 (s, 2H, 2NH, D<sub>2</sub>O exchangeable), 5.87 (m, 2H, 2 =CH), 5.17, 4.98 (dd, 4H, 2=CH<sub>2</sub>), 4.61 (d, 4H, 2NCH<sub>2</sub>), 2.51 (t, 4H, 2CH<sub>2</sub>), 1.72 (p, 4H, 2CH<sub>2</sub>).

*Bis-(4-phenyl-5-mercapto-1,2,4-triazol-3-yl)butane (3c)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 13.60 (s, 2H, NH, D<sub>2</sub>O exchangeable), 7.55-7.33 (m, 10H, Aromatic H), 2.32 (t, 2H, 2CH<sub>2</sub>), 1.38 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 167.6 (2C=S), 151.7 (2C=N), 133.6-128.2 (12 Aromatic C), 24.6 (2CH<sub>2</sub>), 24.1 (2CH<sub>2</sub>).

*General procedure for the synthesis of 5a-n, 8a-l, 12a-f, 15 and 16a-c*

Compounds **3a-c**, **7a-b**, **11**, **14** and **15** (respectively for the synthesis of **5a-n**, **8a-l**, **12a-f**, **15** and **16a-c**) (0.01 mol) were dissolved in aqueous methanol (80:20, methanol:water; 200 mL) containing potassium hydroxide (0.02 mol). A solution of 1,ω-dihaloalkane (0.01 mol) in methanol was added dropwise for an hour. This reaction mixture was then refluxed with stirring on a magnetic stirrer for eight hours. On cooling it to 10-15 °C, a solid separated out. This solid was then separated by filtration, washed with cold water and recrystallised from aqueous dimethyl formamide (DMF).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-7,9-dithia-1,6(3,5)-di-(1,2,4-triazola) cyclononaphane (5a)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.70 (s, 2H, -CH<sub>2</sub>), 3.91 (q, 4H, 2NCH<sub>2</sub>), 2.61 (t, 4H, 2CH<sub>2</sub>), 2.10 (p, 4H, 2CH<sub>2</sub>), 1.16 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 155.6 (2S-C=N), 146.6 (2CH<sub>2</sub>-C=N), 40.7 (CH<sub>2</sub>), 39.2 (2NCH<sub>2</sub>), 25.9 (2CH<sub>2</sub>), 25.0 (2CH<sub>2</sub>), 15.7 (2CH<sub>3</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-7,10-dithia-1,6(3,5)-di-(1,2,4-triazola) cyclodecaphane (5b)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.10 (t, 4H, 2SCH<sub>2</sub>), 3.76 (q, 4H, 2NCH<sub>2</sub>), 3.03 (t, 4H, 2CH<sub>2</sub>), 2.49 (p, 4H, 2CH<sub>2</sub>), 1.30 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 156.3 (2S-C=N), 147.0 (2CH<sub>2</sub>-C=N), 39.1 (2NCH<sub>2</sub>), 32.1 (1SCH<sub>2</sub>), 24.7 (2CH<sub>2</sub>), 23.1 (2CH<sub>2</sub>), 15.3 (2CH<sub>3</sub>). MS (DI) (*m/z*): 338 (M<sup>+</sup>).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-7,11-dithia-1,6(3,5)-di-(1,2,4-triazola) cycloundecaphane (5c)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.87 (q, 4H, 2NCH<sub>2</sub>), 3.31 (t, 4H, 2SCH<sub>2</sub>), 2.76 (t, 4H, 2CH<sub>2</sub>), 2.10 (p, 2H, 1CH<sub>2</sub>), 1.95 (p, 4H, 2CH<sub>2</sub>), 1.30 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.5 (2S-C=N), 149.6 (2CH<sub>2</sub>-C=N), 39.8 (2NCH<sub>2</sub>), 36.2 (2SCH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 25.9 (2CH<sub>2</sub>), 24.3 (2CH<sub>2</sub>), 15.4 (2CH<sub>3</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-7,12-dithia-1,6(3,5)-di-(1,2,4-triazola) cyclododecaphane (5d)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.86 (q, 4H, 2NCH<sub>2</sub>), 3.20 (t, 4H, 2SCH<sub>2</sub>), 2.72 (t, 4H, 2CH<sub>2</sub>), 2.03 (p, 4H, 2CH<sub>2</sub>), 1.84 (p, 4H, 2CH<sub>2</sub>), 1.28 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 154.8 (2S-C=N), 149.7 (2CH<sub>2</sub>-C=N), 38.6 (2NCH<sub>2</sub>), 32.5 (2SCH<sub>2</sub>), 28.4 (2CH<sub>2</sub>), 26.3 (2CH<sub>2</sub>), 24.6 (2CH<sub>2</sub>), 15.3 (2CH<sub>3</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-7,13-dithia-1,6(3,5)-di-(1,2,4-triazola) cyclotridecaphane (5e)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.87 (q, 4H, 2NCH<sub>2</sub>), 3.19 (t, 4H, 2SCH<sub>2</sub>), 2.76 (t, 4H, 2CH<sub>2</sub>), 1.94 (p, 4H, 2CH<sub>2</sub>), 1.75 (p, 4H, 2CH<sub>2</sub>), 1.52 (p, 2H, 1CH<sub>2</sub>), 1.25 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 154.8 (2S-C=N), 149.9 (2CH<sub>2</sub>-C=N), 38.6 (2NCH<sub>2</sub>), 32.9 (2SCH<sub>2</sub>), 28.2 (2CH<sub>2</sub>), 26.3 (2CH<sub>2</sub>), 24.6 (1CH<sub>2</sub>), 24.1 (2CH<sub>2</sub>), 15.3 (2CH<sub>3</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diallyl-7,9-dithia-1,6(3,5)-di-(1,2,4-triazola) cyclononaphane (5f)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 5.80 (m, 2H, 2 =CH), 5.21 (dd, 4H, 2 =CH<sub>2</sub>), 4.73 (s, 2H, 1CH<sub>2</sub>), 4.69 (d, 4H, 2NCH<sub>2</sub>), 2.58 (t, 4H, 2CH<sub>2</sub>), 2.10 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 155.9 (2S-C=N), 147.4 (2C-C=N), 131.0 (2C=CH), 118.3 (2C=CH<sub>2</sub>), 46.1 (SCH<sub>2</sub>), 40.7 (2NCH<sub>2</sub>), 25.4 (2CH<sub>2</sub>), 21.8 (2CH<sub>2</sub>).



*1<sup>4</sup>,6<sup>4</sup>-Diallyl-7,11-dithia-1,6(3,5)-di-(1,2,4-triazola)cycloundecaphane (5g)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 5.81 (m, 2H, 2=CH), 5.19 (dd, 4H, 2 =CH<sub>2</sub>), 4.55 (d, 4H, 2NCH<sub>2</sub>), 3.24 (t, 4H, 2CH<sub>2</sub>), 2.73 (t, 4H, 2CH<sub>2</sub>), 1.98 (p, 2H, 1CH<sub>2</sub>), 1.89 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 155.4 (2S-C=N), 149.4 (2C-C=N), 131.3 (2C=CH), 117.8 (2C=CH<sub>2</sub>), 45.8 (2CH<sub>2</sub>), 32.1 (2NCH<sub>2</sub>), 29.3 (2CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 24.2 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diallyl-7,12-dithia-1,6(3,5)-di-(1,2,4-triazola)cyclododecaphane (5h)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 5.82 (m, 2H, 2=CH), 5.10 (dd, 4H, 2 =CH<sub>2</sub>), 4.58 (d, 4H, 2NCH<sub>2</sub>), 3.13 (t, 4H, 2CH<sub>2</sub>), 2.50 (t, 4H, 2CH<sub>2</sub>), 2.01 (p, 4H, 1CH<sub>2</sub>), 1.72 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 155.5 (2S-C=N), 149.1 (2C-C=N), 131.1 (2C=CH), 117.9 (2C=CH<sub>2</sub>), 45.7 (2SCH<sub>2</sub>), 32.6 (2NCH<sub>2</sub>), 28.4 (2CH<sub>2</sub>), 23.8 (2CH<sub>2</sub>), 23.5 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diallyl-7,13-dithia-1,6(3,5)-di-(1,2,4-triazola)cyclotridecaphane (5i)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 5.82 (m, 2H, 2=CH), 5.07 (dd, 4H, 2=CH<sub>2</sub>), 4.24 (d, 4H, 2NCH<sub>2</sub>), 3.35 (t, 4H, 2CH<sub>2</sub>), 2.66 (t, 4H, 2CH<sub>2</sub>), 1.90 (p, 4H, 1CH<sub>2</sub>), 1.72 (p, 4H, 2CH<sub>2</sub>), 1.58 (p, 2H, 1CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 155.2 (2S-C=N), 150.4 (2C-C=N), 131.8 (2C=CH), 117.8 (2C=CH<sub>2</sub>), 45.5 (2CH<sub>2</sub>), 33.1 (2NCH<sub>2</sub>), 28.9 (2CH<sub>2</sub>), 28.1 (2CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 24.5 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diphenyl-7,9-dithia-1,6(3,5)-di-(1,2,4-triazola)cyclononaphane (5j)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.52-7.77 (m, 10H, Aromatic H), 4.64 (s, 2H, CH<sub>2</sub>), 2.52 (t, 4H, 2CH<sub>2</sub>), 2.00 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 157.0 (2S-C=N), 148.8 (2C-C=N), 133.3-127.6 (12 Aromatic C), 41.5 (CH<sub>2</sub>), 25.0 (2CH<sub>2</sub>), 22.3 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diphenyl-7,10-dithia-1,6(3,5)-di-(1,2,4-triazola)cyclodecaphane (5k)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.63-7.55 (m, 10H, Aromatic H), 2.86 (t, 4H, 2CH<sub>2</sub>), 2.64 (t, 4H, 2CH<sub>2</sub>), 1.96 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 158.0 (2S-C=N), 148.8 (2C-C=N), 133.3-127.9 (12 Aromatic C), 32.1 (2CH<sub>2</sub>), 25.1 (2CH<sub>2</sub>), 23.1 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diethyl-9(1,2)-benzena-7,11-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cycloundecaphane (5l)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.73-6.95 (m, 4H, Aromatic H), 4.72 (s, 4H, 2SCH<sub>2</sub>), 3.80 (q, 4H, 2NCH<sub>2</sub>), 2.76 (t, 4H, 2CH<sub>2</sub>), 2.00 (p, 4H, 2CH<sub>2</sub>), 1.17 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 155.5 (2S-C=N), 149.6 (2C-C=N), 133.0-125.0 (6 Aromatic C), 45.7 (2SCH<sub>2</sub>), 36.0 (2NCH<sub>2</sub>), 25.9

(2CH<sub>2</sub>), 24.6 (2CH<sub>2</sub>), 15.4 (2CH<sub>3</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diallyl-9(1,2)-benzena-7,11-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cycloundecaphane (5m)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.63-7.04 (m, 4H, Aromatic H), 5.74 (m, 2H, 2C=CH), 5.16 (dd, 4H, 2C=CH<sub>2</sub>), 4.73 (s, 4H, 2SCH<sub>2</sub>), 4.38 (d, 4H, 2NCH<sub>2</sub>), 2.71 (t, 4H, 2CH<sub>2</sub>), 1.72 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 155.5 (2S-C=N), 149.6 (2C-C=N), 133.0-125.0 (6 Aromatic C), 131.2 (2C=CH), 117.8 (2C=CH<sub>2</sub>), 45.7 (2SCH<sub>2</sub>), 36.0 (2NCH<sub>2</sub>), 25.9 (2CH<sub>2</sub>), 24.6 (2CH<sub>2</sub>).

*1<sup>4</sup>,6<sup>4</sup>-Diphenyl-9(1,2)-benzena-7,11-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cycloundecaphane (5n)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.65-7.15 (m, 14H, Aromatic H), 4.82 (s, 4H, 2SCH<sub>2</sub>), 2.69 (t, 4H, 2CH<sub>2</sub>), 2.03 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 158.0 (2S-C=N), 148.8 (2C-C=N), 133.3-127.9 (18 Aromatic C), 38.0 (2SCH<sub>2</sub>), 25.1 (2CH<sub>2</sub>), 23.2 (2CH<sub>2</sub>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)-benzena-4,7-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cycloheptaphane (9a)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.58-7.22 (m, 14H, Aromatic H), 3.46 (t, 4H, 2SCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 153.6, 151.3 (4C=N), 133.4-127.0 (18x Aromatic C), 31.8 (2SCH<sub>2</sub>). MS (DI) (*m/z*): 454 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)-benzena-4,8-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclooctaphane (9b)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.68-7.28 (m, 14H, Aromatic H), 3.23 (t, 4H, 2SCH<sub>2</sub>), 1.96 (p, 2H, CH<sub>2</sub>). MS (DI) (*m/z*): 468 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)-benzena-4,9-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclononaphane (9c)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.55-7.19 (m, 14H, Aromatic H), 3.13 (t, 4H, 2SCH<sub>2</sub>), 1.73 (p, 4H, 2CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 153.4, 152.0 (4C=N), 133.5-124.8 (18 Aromatic C), 35.7 (2SCH<sub>2</sub>), 31.4 (2CH<sub>2</sub>). MS (DI) (*m/z*): 482 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)-benzena-4,10-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclodecaphane (9d)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.51-7.21 (m, 14H, Aromatic H), 3.05 (t, 4H, 2SCH<sub>2</sub>), 1.64 (p, 4H, 2CH<sub>2</sub>), 1.33 (p, 2H, CH<sub>2</sub>). MS (DI) (*m/z*): 496 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-4,7-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cycloheptaphane (9e)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 7.63-6.90 (m, 12H, Aromatic

H), 5.52 (t, 4H, 2SCH<sub>2</sub>), 1.90 (s, 3H, CH<sub>3</sub>), 1.85 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): 151.0, 149.0 (4C=N), 135.6-118.7 (18 Aromatic C), 41.9, 31.4 (2SCH<sub>2</sub>), 17.4, 17.3 (2CH<sub>3</sub>). MS (DI) (*m/z*): 482 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-4,8-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cyclooctaphane (9f)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.32-7.13 (m, 12H, Aromatic H), 3.76 (t, 4H, 2SCH<sub>2</sub>), 2.06 (p, 2H, CH<sub>2</sub>), 1.92 (s, 3H, CH<sub>3</sub>), 1.87 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.8, 152.6 (4C=N), 135.6-126.5 (18 Aromatic C), 30.8, 30.6 (2SCH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 17.7, 17.4 (2CH<sub>3</sub>). MS (DI) (*m/z*): 496 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-4,9-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cyclononaphane (9g)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.80-7.09 (m, 12H, Aromatic H), 3.31 (t, 4H, 2SCH<sub>2</sub>), 1.93 (s, 3H, CH<sub>3</sub>), 1.85 (p, 4H, 2CH<sub>2</sub>), 1.80 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.8, 153.1 (4C=N), 135.6-127.4 (18x Aromatic C), 31.4, 31.3 (2SCH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 17.5, 17.4 (2CH<sub>3</sub>). MS (DI) (*m/z*): 510 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-4,10-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cyclodecaphane (9h)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.60-7.12 (m, 12H, Aromatic H), 3.21 (t, 4H, 2SCH<sub>2</sub>), 1.91 (s, 3H, CH<sub>3</sub>), 1.89 (s, 3H, CH<sub>3</sub>), 1.68 (q, 4H, 2CH<sub>2</sub>), 1.55 (p, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.8, 153.2 (4C=N), 135.5-127.4 (18 Aromatic C), 32.2, 31.8 (2SCH<sub>2</sub>), 28.7, 27.2 (3CH<sub>2</sub>), 17.3 (CH<sub>3</sub>). MS (DI) (*m/z*): 524 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)6(1,2)-dibenzena-4,8-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclooctaphane (9i)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>) δ 7.57-7.05 (m, 14H, Aromatic H), 4.53 (s, 4H, 2SCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 154.4, 152.4 (4C=N), 135.9-127.8 (24 Aromatic C), 34.7 (2SCH<sub>2</sub>). MS (DI) (*m/z*): 530 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-4,8-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cyclooctaphane (9j)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.23-6.95 (m, 12H, Aromatic H), 4.76 (s, 2H, SCH<sub>2</sub>), 4.40 (s, 2H, SCH<sub>2</sub>), 1.96 (s, 3H, CH<sub>3</sub>), 1.89 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.9, 151.3 (4C=N), 134.4-126.3 (18 Aromatic C), 33.4, 33.1, (2SCH<sub>2</sub>), 16.5, 16.2 (2CH<sub>3</sub>). MS (DI) (*m/z*): 558 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Diphenyl-2(1,3)-benzena-7-oxa-4,10-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclodecaphane (9k)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.51-7.22 (m, 14H, Aromatic H), 3.70 (t, 4H, 2OCH<sub>2</sub>), 3.64 (t, 4H, 2SCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.5, 152.0 (4C=N), 133.5-127.0 (18 Aromatic C), 70.2 (2 OCH<sub>2</sub>), 43.4 (2SCH<sub>2</sub>). MS (DI) (*m/z*): 498 (M<sup>+</sup>).

*1<sup>4</sup>,3<sup>4</sup>-Di-[(2'-methyl)phenyl]-2(1,3)6(1,2)-dibenzena-7-oxa-4,10-dithia-1(3,5)3(5,3)-di-(1,2,4-triazola)cyclodecaphane (9l)*

<sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 7.59-7.10 (m, 16H, Aromatic H), 3.90-3.44 (m, 8H, 2OCH<sub>2</sub> & 2SCH<sub>2</sub>), 1.87 (s, 3H, -CH<sub>3</sub>), 1.85 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 153.8, 152.9 (4C=N), 135.5-126.4 (24 Aromatic C), 70.1, 69.1 (2OCH<sub>2</sub>), 42.6, 31.4 (2SCH<sub>2</sub>), 17.4, 17.3 (2CH<sub>3</sub>). MS (DI) (*m/z*): 526 (M<sup>+</sup>).

*1<sup>4</sup>5<sup>4</sup>-Diethyl-3(1,3)-benzena-2,4-dioxa-6,8-dithia-1,5(3,5)(5,3)-di-(1,2,4-triazola)cyclooctaphane (12a)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25-6.64 (m, 4H, Aromatic H), 5.10 (s, 4H, 2OCH<sub>2</sub>), 4.70(s, 2H, 1CH<sub>2</sub>), 4.02 (q, 4H, 2NCH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.5, 147.8 (4C=N), 158.6, 112.4, 107.9, 102.1 (6 Aromatic C), 62.4 (CH<sub>2</sub>), 60.3 (2OCH<sub>2</sub>), 39.7 (2NCH<sub>2</sub>), 15.2 (2CH<sub>3</sub>).

*1<sup>4</sup>5<sup>4</sup>-Diethyl-3(1,3)-benzena-2,4-dioxa-6,9-dithia-1,5(3,5)(5,3)-di-(1,2,4-triazola)cyclononaphane (12b)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25-6.64 (m, 4H, Aromatic H), 5.15 (s, 4H, 2OCH<sub>2</sub>), 4.02 (q, 4H, 2NCH<sub>2</sub>), 3.10 (t, 4H, 2SCH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.5, 147.8 (2C=N), 158.6, 112.4, 107.9, 102.1 (6 Aromatic C), 60.3 (2OCH<sub>2</sub>), 39.7 (2NCH<sub>2</sub>), 37.2 (2SCH<sub>2</sub>), 15.2 (2CH<sub>3</sub>).

*1<sup>4</sup>5<sup>4</sup>-Diethyl-3(1,3)-benzena-2,4-dioxa-6,10-dithia-1,5(3,5)(5,3)-di-(1,2,4-triazola)cyclodecaphane (12c)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25-6.64 (m, 4H, Aromatic H), 5.21 (s, 4H, 2OCH<sub>2</sub>), 4.10 (q, 4H, 2NCH<sub>2</sub>), 3.62 (t, 4H, 2SCH<sub>2</sub>), 3.02 (p, 2H, 1CH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.1, 145.5 (4C=N), 157.3, 124.9, 105.4, 102.5 (6 Aromatic C), 55.4 (2OCH<sub>2</sub>), 33.9 (2NCH<sub>2</sub>), 27.2 (2SCH<sub>2</sub>), 25.7 (1CH<sub>2</sub>), 10.2 (2CH<sub>3</sub>).

*1<sup>4</sup>5<sup>4</sup>-Diethyl-3(1,3)-benzena-2,4-dioxa-6,11-dithia-1,5(3,5)(5,3)-di-(1,2,4-triazola)cycloundecaphane (12d)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25-6.64 (m, 4H, Aromatic H), 5.21 (s, 4H, 2OCH<sub>2</sub>), 4.10 (q, 4H, 2NCH<sub>2</sub>), 3.01 (t, 4H, 2SCH<sub>2</sub>), 1.72 (p, 4H, 2CH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.0, 150.8 (4C=N), 157.3, 130.2, 110.0, 104.0 (6 Aromatic C), 60.6 (2OCH<sub>2</sub>), 39.2 (2NCH<sub>2</sub>), 32.8 (2SCH<sub>2</sub>), 27.8 (2CH<sub>2</sub>), 15.2(2CH<sub>3</sub>).



*1<sup>4</sup>,5<sup>4</sup>-Diethyl-3(1,3)-benzena-2,4-dioxa-6,12-dithia-1,5(3,5)(5,3)-di-(1,2,4-triazola)cyclododecaphane (12e)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.25-6.64 (m, 4H, Aromatic H), 5.20 (s, 4H, 2OCH<sub>2</sub>), 4.10 (q, 4H, 2NCH<sub>2</sub>), 3.01 (t, 4H, 2SCH<sub>2</sub>), 1.40-1.32 (m, 6H, 3CH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.1, 150.7 (4C=N), 157.3, 130.2, 108.8, 103.5 (6 Aromatic C), 59.8 (2OCH<sub>2</sub>), 39.3 (2NCH<sub>2</sub>), 34.0, 29.0 (4SCH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 15.4 (2CH<sub>3</sub>).

*1<sup>4</sup>,5<sup>4</sup>-Diphenyl-3(1,3)8(1,2)dibenzena-2,4-dioxa-6,10-dithia-1,3(3,5)(5,3)-di-(1,2,4-triazola)cyclodecaphane (12f)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.36-6.61 (m, 8H, Aromatic H), 5.10 (s, 4H, 2OCH<sub>2</sub>), 4.64 (s, 4H, 2SCH<sub>2</sub>), 3.98 (q, 4H, 2NCH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.1, 147.8 (4C=N), 158.6, 134.7-125.7, 107.9, 101.9 (12 Aromatic C), 60.4 (2OCH<sub>2</sub>), 39.5 (2NCH<sub>2</sub>), 37.2 (2SCH<sub>2</sub>), 15.1 (2CH<sub>3</sub>).

*1,3-Di-[4-anilino-5(2'-hydroxyphenyl)-1,2,4-triazol-3-yl]mercapto propane (15)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 11.12 (s, 2H, 2OH, D<sub>2</sub>O exchangeable), 7.84-6.94 (m, 18H, Aromatic H), 5.72 (s, 2H, 2NH, D<sub>2</sub>O exchangeable), 3.42 (t, 4H, 2SCH<sub>2</sub>), 2.32 (p, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.3 (2S-C=N), 153.4 (2C=N), 156.2-113.2 (24 Aromatic C), 30.4 (2SCH<sub>2</sub>), 28.5 (-CH<sub>2</sub>).

*1<sup>4</sup>,9<sup>4</sup>-Dianilino-2,8(1,2)-dibenza-3,7-dioxa-10,14-dithia-1(3,5)9(5,3)-di-(1,2,4-triazola)cyclotetradecaphane (16a)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.68-6.74 (m, 18H, Aromatic H), 5.87 (s, 2H, 2NH), 4.18 (t, 4H, 2OCH<sub>2</sub>), 3.62 (t, 4H, 2SCH<sub>2</sub>), 2.41 (p, 2H, CH<sub>2</sub>), 2.23 (p, 2H, CH<sub>2</sub>). MS (DI) (*m/z*): 648 (M<sup>+</sup>).

*1<sup>4</sup>,10<sup>4</sup>-Dianilino-2,9(1,2)-dibenza-3,8-dioxa-11,15-dithia-1(3,5)10(5,3)-di-(1,2,4-triazola)cyclopentadecaphane (16b)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.86-7.10 (m, 18H, Aromatic H), 5.72 (s, 2H, 2NH), 3.82 (s, 4H, 2OCH<sub>2</sub>), 3.42 (t, 4H, SCH<sub>2</sub>), 2.34 (p, 2H, CH<sub>2</sub>), 2.06 (m, 4H, 2CH<sub>2</sub>).

*1<sup>4</sup>,9<sup>4</sup>-Dianilino-3,7-dioxa-10,14-dithia-1(3,5)9(5,3)-di-(1,2,4-triazola)-2,5,8(1,2)-tribenza cyclotetradecaphane (16c)*

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.83-6.81 (m, 22H, Aromatic H), 5.72 (s, 2H, 2NH), 4.62 (s, 4H, 2OCH<sub>2</sub>), 3.42 (t, 4H, 2SCH<sub>2</sub>), 2.32 (p, 2H, CH<sub>2</sub>).

*General procedure for the synthesis of 8a-b*

Isophthalic acid dihydrazide (0.01 mol) and phenyl or *o*-tolyl isothiocyanate (0.02 mol) were refluxed in methanol

(50 mL) for 4h. The compound formed was filtered, washed with water, was added to 10% aqueous alkali (100 mL) and heated on water bath for 4h. The reaction mixture was poured over crushed ice. This cold solution was then filtered to remove some trace particles. Obtained filtrate was neutralized with dilute aqueous hydrochloric acid to obtain a solid compound, which was filtered, washed with cold water and recrystallised from aqueous DMF.

*1,3-Bis-(5-mercapto-4-phenyl-1,2,4-triazol-3-yl)benzene (8a)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 14.31 (s, 2H, 2NH), 7.66-7.41 (m, 14H, Aromatic H). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 169.1 (2C=S), 150.0 (2C=N), 134.5-126.6 (18 Aromatic C). MS (DI) (*m/z*): 428 (M<sup>+</sup>).

*1,3-Bis-[5-mercapto-4-(2'-methyl)phenyl-1,2,4-triazol-3-yl]benzene (8b)*

<sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 14.18 (s, 2H, 2NH), 7.39-7.18 (m, 12H, Aromatic H), 1.91 (s, 6H, 2CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): δ 168.2 (2C=S), 149.3 (2C=N), 17.2 (2CH<sub>3</sub>), 135.7-126.2 (18 Aromatic C). MS (DI) (*m/z*): 456 (M<sup>+</sup>).

*Synthesis of 1,3-bis-[(4-ethyl-3-mercapto-1,2,4-triazol-3-yl)methyleneoxy]benzene (11)*

Benzene-1,3-dioxyacetic acid **10** (2.26 g, 0.01 mol) and 4-ethyl-3-thiosemicarbazide **2a** (2.38 g, 0.02 mol) were thoroughly mixed using mortar and pestle. This mixture was then fused in oil-bath maintaining temperature 140 °C for 4h. The reaction mixture was then cooled and dumped into ice. The resulting brown colored solid filtered off, washed with 5% sodium bicarbonate solution followed by water till pH becomes neutral and recrystallized from aqueous DMF, 3.13 g (85%), mp 184 °C; <sup>1</sup>H NMR (DMSO *d*<sub>6</sub>): δ 13.80 (s, 2H, 2x-NH), 7.28-6.72 (m, 4H, Aromatic H), 5.23 (s, 4H, 2OCH<sub>2</sub>), 4.01 (q, 4H, 2NCH<sub>2</sub>), 1.26 (t, 6H, 2CH<sub>3</sub>).

*General procedure for the synthesis of 4-anilino-5-(2'-hydroxyphenyl)-3-mercapto-1,2,4-triazole (14)*

Salicylic acid hydrazide **13** (1.52 g, 0.01 mol) was dissolved in ethanol (40 mL) in the presence of potassium hydroxide (1.12 g, 0.02 mol) and cooled at 5 °C. To this cold solution carbon disulphide (1.14 g, 0.015 mol) was added under stirring. The precipitated dithiocarbamate salt intermediate was filtered off, washed with petroleum ether and dried. This salt was fused with phenylhydrazine (1.08 g, 0.01 mol) at 140 °C for 6h. The reaction mixture was then poured onto cold water and filtered to remove traces of inorganic material. The filtrate was neutralized with dilute

aqueous hydrochloric acid till pH of the solution became neutral. The resulting pale yellow solid was filtered off, washed with cold water and recrystallized from aqueous DMF. <sup>1</sup>H NMR (DMSO d<sub>6</sub>): δ 13.84 (s, 1H, S=C-NH, D<sub>2</sub>O exchangeable), 10.28 (s, 1H, OH, D<sub>2</sub>O exchangeable), 7.43-6.84 (m, 9H, Aromatic H), 5.82 (s, 1H, NH, D<sub>2</sub>O exchangeable). <sup>13</sup>C NMR (DMSO d<sub>6</sub>): δ 164.2 (2C=S), 148.2 (2 C=N), 154.3-113.1 (12 Aromatic C).

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## Supplementary Information

<sup>1</sup>H NMR, <sup>13</sup>C NMR data is available free of charge at <http://jbc.sbq.org.br>, as PDF file.

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