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EFFECTIVE SYNTHESIS OF *N*-ARYL-SUBSTITUTED 1,5,3-DITHIAZEPINANES AND 1,5,3-DITHIAZOCINANES

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Selective methods were developed for the synthesis of N-aryl-1,5,3-dithiazepinanes and N-aryl-1,5,3-dithiazocinanes by transamination of N-tert-butyl-1,5,3-dithiazepinane or recyclization of 1-oxa-3,6-dithiacycloheptane and 1-oxa-3,7-dithiacyclooctane by the action of aniline derivatives in the presence of $Sm(NO_3)_3 \cdot 6H_2O$ catalyst.

Keywords: arylamines, *N*-aryl-1,5,3-dithiazepinanes, *N*-aryl-1,5,3-dithiazocinanes, *N*-*tert*-butyl-1,5,3-dithiazepinane, 1-oxa-3,6-dithiacycloheptane, 1-oxa-3,7-dithiacyclooctane, catalysis, recyclization, transamination.

Heterocyclic compounds containing nitrogen and sulfur atoms and belonging to the 1,3,5-dithiazinane, 1,3,5-thiadiazinane, and 1,5,3-dithiazepinane systems [1-8] have a set of useful properties [9-14] and are promising for extensive practical application.

According to data in [15], *N*-alkyl-1,5,3-dithiazepinanes can be obtained by a three-component condensation of 1,2-ethanedithiol, formaldehyde, and hydroxylamine or by reaction of 5-(*tert*-butyl)-2-oxohexahydro-1,3,5-triazine with 1,2-ethanedithiol in the presence of $BF_3 \cdot 2AcOH$ [16]. There are no published data on the preparation of *N*-aryl-1,5,3-dithiazepinanes.

In order to develop a new preparative method for the synthesis of *N*-aryl-1,5,3-dithiazepinanes with various structures, we investigated the reaction of *N*-*tert*-butyl-1,5,3-dithiazepinane and 1-oxa-3,6-dithiacycloheptane with isomeric aminophenols, aminothiophenols, and phenylenediamines by analogy with our previously investigated catalytic transamination of *N*-methyl-1,3,5-dithiazinane by anilines [17].

Preliminary experiments indicated that among the tested salts and complexes of Fe, Co, Ti, Zr, Ni, Pd, Sm, and Yb [17] the most active in the catalytic transamination of *N*-*tert*-butyl-1,5,3-dithiazepinane with the above-mentioned arylamines is $Sm(NO_3)_3 \cdot 6H_2O$. All the subsequent experiments were therefore conducted with this catalyst.

We established that under the developed conditions (5 mol% of $Sm(NO_3)_3 \cdot 6H_2O$, 20°C, 3 h, EtOH–$CHCl_3$), *o*- and *p*-aminophenols react with an equimolar amount of *N*-*tert*-butyl-1,5,3-dithiazepinane (**1**) or 1-oxa-3,6-dithiacycloheptane (**2**) with the selective formation of 2- (**3**) and 4-(1,5,3-dithiazepinan-3-yl)-

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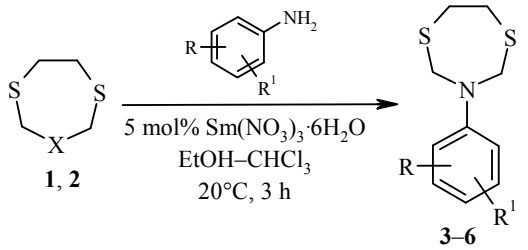
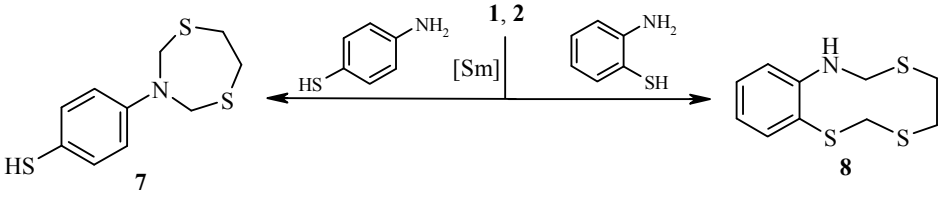
phenols (**4**) in yields of 51-85%. Under our chosen reaction conditions, *m*-aminophenol forms poorly soluble compounds the identification of which has so far been difficult. In the absence of the catalyst, the selectivity of the reaction is reduced, and the yield of the desired heterocycles **3** and **4** does not exceed 30%.

In the case of *p*-aminobenzoic and 5-aminosalicylic acids, we established that they react with an equimolar amount of *N*-*tert*-butyl-1,5,3-dithiazepinane (**1**) or 1-oxa-3,6-dithiacycloheptane (**2**) under the developed conditions, selectively forming 4-(1,5,3-dithiazepinan-3-yl)benzoic acid (**5**) or 5-(1,5,3-dithiazepinan-3-yl)-2-hydroxybenzoic acid (**6**), respectively, with yields of 57-76%.



1 X = *t*-BuN; **2** X = O; **3** R = 2-OH, R^1 = H; **4** R = 4-OH, R^1 = H;
5 R = 4-CO_2H, R^1 = H; **6** R = 4-OH, R^1 = 5-CO_2H

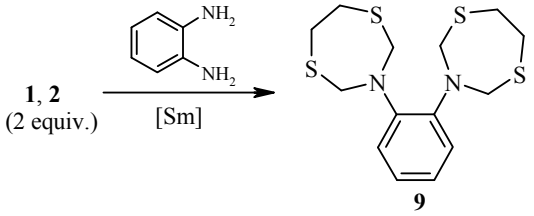
In the reaction of *p*- and *o*-aminothiophenols with an equimolar amount of the dithiazepinane **1** or oxadithiacycloheptane **2** under the above-mentioned conditions, 4-(1,5,3-dithiazepinan-3-yl)thiophenol (**7**) and 1,3,6,8-benzotrithiazecinane (**8**) are formed with high selectivity and with yields of 48-74%. In the absence of catalyst this reaction proceeds nonselectively, with low yields of the targeted heterocycles **7** and **8**.



The ^{1}H NMR spectra of compounds **3-7** are characterized by broad signals of equal intensity in the regions of 3.06-3.08 and 4.55-4.86 ppm, belonging to the methylene protons situated between the two sulfur atoms and between the sulfur and nitrogen atoms, respectively.

The structures of the new *N*-aryl-1,5,3-dithiazepinanes **3-7** and 1,3,6,8-benzotrithiazecinane (**8**) were established unambiguously on the basis of 2D NMR spectroscopy methods (COSY, NOESY, HSQC, HMBC), and also by MALDI TOF mass spectrometry.

o-Phenylenediamine reacts with compounds **1** and **2** under the same conditions in a molar ratio of 1:2 with the selective formation of 3,3'-(1,2-phenylene)bis-1,5,3-dithiazepinane (**9**) with yields of 43 and 65%, respectively. *o*-Phenylenediamine does not enter into the reaction in the absence of catalyst.



Under the conditions of the reaction, we could not rule out the possibility of formation of a structural isomer, the heterocycle **9'** (Fig. 1). The choice between the heterocycles **9** and **9'** was based on conformation analysis. Thus, the presence of the *o*-phenylene bridge between the nitrogen atoms fixes the conformational rigidity of the probable structure **9'**, in which the diastereotopic protons of the methylene bond between the nitrogen and sulfur atoms must be distinguished due to the steric and anisotropic effects of the aromatic ring. The presence of a singlet signal for the methylene group at 4.78 ppm in the ^{1}H NMR spectrum demonstrates unambiguously the equivalence of the methylene protons of the N─CH_2─S group and the conformational mobility of the seven-membered fragments of the molecule characteristic of structure **9**. Thus, the formation of 3,3'-(1,2-phenylene)bis-1,5,3-dithiazepinane (**9**) is observed under our chosen conditions.

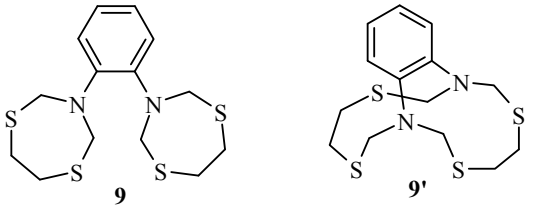
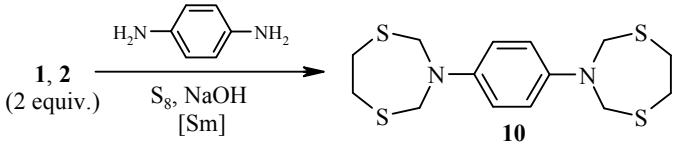
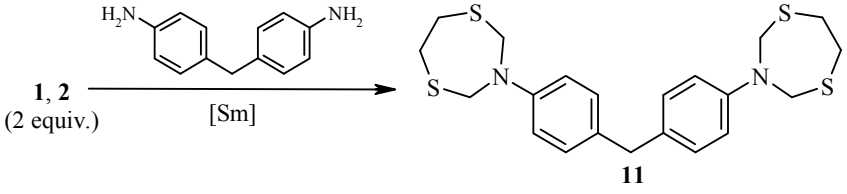


Fig. 1. The structural isomers of the heterocycle **9**.

Under the above-mentioned reaction conditions, *m*-phenylenediamine gives poorly soluble heterocyclic compounds, while *p*-phenylenediamine does not enter into the reaction. To activate the N─H bond in *p*-phenylenediamine we used the S_8+NaOH reagent [18]. The initiating action of the sulfur arises from the fact that the amine molecule solvates the sulfide ions generated from the sulfur and alkali with the formation of a charge separation complex. It was found that *p*-phenylenediamine in the presence of this reagent reacts effectively with *N-tert*-butyl-1,5,3-dithiazepinane (**1**) or 1-oxa-3,6-dithiacycloheptane (**2**) under the chosen conditions with selective formation of 3,3'-(1,4-phenylene)bis-1,5,3-dithiazepinane (**10**) with yields of 45 and 66%.

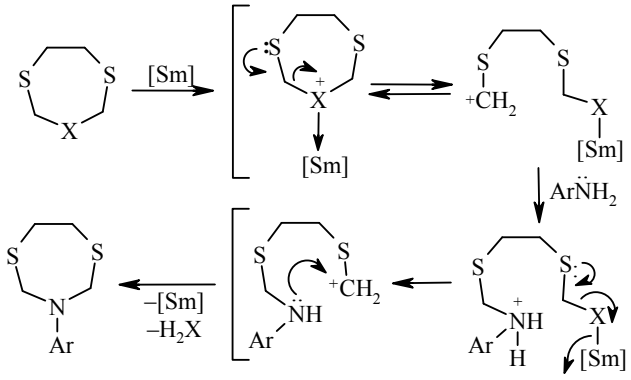


Unlike *p*-phenylenediamine, 4,4'-diaminodiphenylmethane reacts with compounds **1** or **2** without previous activation, leading to a selective formation of 3,3'-[methylenebis(1,4-phenylene)]bis-1,5,3-dithiazepinane (**11**) with yields of 52 and 67%.



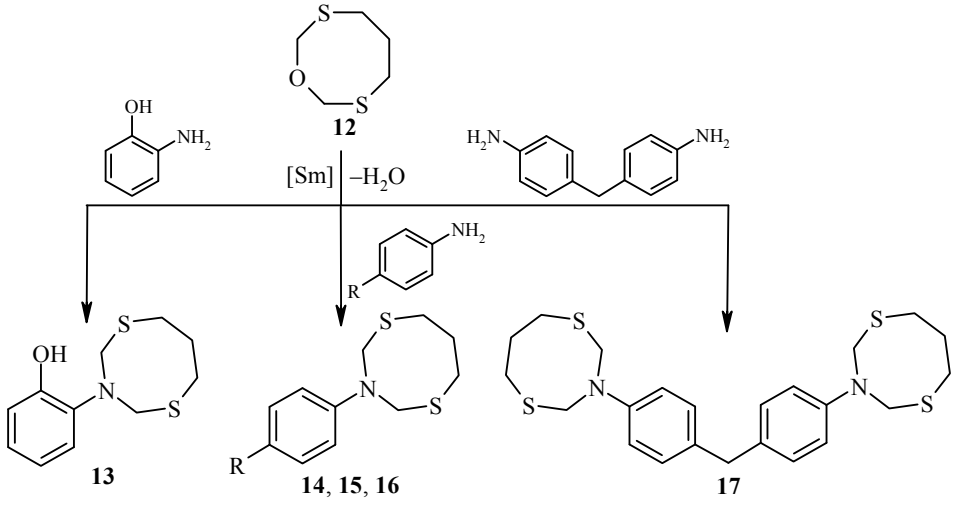
The probable mechanism of the catalytic transamination of *N-tert*-butyl-1,5,3-dithiazepinane (**1**) or recyclization of 1-oxa-3,6-dithiacycloheptane (**2**) with the participation of aniline derivatives includes opening of the initial heterocycles, nucleophilic addition of arylamines to the carbocation, and intramolecular cyclization with formation of the desired heterocycles [19-23].

The obtained results on the synthesis of *N*-aryl-1,5,3-dithiazepinanes made it possible to undertake investigations directed at the development of methods for the preparation of *N*-aryl-1,5,3-dithiazocinanes by catalytic recyclization of 1-oxa-3,7-dithiacyclooctane (**12**) with arylamines.



X = *t*-BuN, O; [Sm] = $Sm(NO_3)_3 \cdot 6H_2O$

It was established that *o*- and *p*-aminophenols, *p*-aminothiophenol, *p*-aminobenzoic acid, and 4,4'-diaminodiphenylmethane enter into a reaction with 1-oxa-3,7-dithiacyclooctane (**12**) with the selective formation of 2- (**13**) and 4-(1,5,3-dithiazocinan-3-yl)phenols (**14**), 4-(1,5,3-dithiazocinan-3-yl)thiophenol (**15**), 4-(1,5,3-dithiazocinan-3-yl)benzoic acid (**16**), and 3,3'-[methylenebis(1,4-phenylene)]bis-1,5,3-dithiazocinane (**17**). With using 5 mol% of $Sm(NO_3)_3 \cdot 6H_2O$ in these reactions, the highest yields (61-83%) of the targeted heterocycles **13-17** were obtained under the conditions described above (20°C, 3 h, solvent $CHCl_3$–EtOH or $CHCl_3$). In the absence of catalyst the yield of the targeted heterocycles did not exceed 20%. The structure of the *N*-aryl-1,5,3-dithiazocinanes **13-17** was established from ^1H and ^{13}C NMR spectra with the use of 2D experiments (COSY, NOESY, HSQC, HMBC) and also from MALDI TOF mass spectrometry.



14 R = OH, **15** R = SH, **16** R = COOH

Thus, the catalytic transamination of *N*-*tert*-butyl-1,5,3-dithiazepinane and recyclization of 1-oxa-3,6-dithiacycloheptane and 1-oxa-3,7-dithiacyclooctane with aniline derivatives makes it possible to synthesize heterocycles of *N*-aryl-1,5,3-dithiazepinane and *N*-aryl-1,5,3-dithiazocinane series with high yields and selectivity.

EXPERIMENTAL

The one-dimensional (^{1}H, ^{13}C), homonuclear (COSY, NOESY), and heteronuclear (HSQC, HMBC) NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz for ^{1}H nuclei, 100 MHz for ^{13}C nuclei) using standard Bruker procedures with TMS as standard. The mixing time for the NOESY experiments was 0.3 sec. The mass spectra were recorded on a Bruker Autoflex III MALDI TOF/TOF instrument. The melting points were determined on a RNMK 80/2617 apparatus. Elemental analysis of the samples was performed on a Carlo Erba 1106 analyzer. The refractive index (n_D^{20}) was determined on an IRF-22 refractometer. The reactions were monitored by TLC on Sorbfil plates (PTSKh-AF-V) with development by I_2 vapor. Silica gel KSK (100-200 μm) was used for column chromatography.

***N-tert*-Butyl-1,5,3-dithiazepinane (1)**. A mixture of a 37% aqueous formalin solution (14.8 ml, 0.2 mol) and 1,2-ethanedithiol (8.3 ml, 0.1 mol) was stirred for 1 h. Then *tert*-butylamine (10.4 ml, 0.1 mol) was added to the reaction mixture dropwise, and the mixture was stirred at 20°C for 3 h. The reaction mixture was extracted with $CHCl_3$, and the extract was evaporated. Yield 12.4 g (65%). The physicochemical and spectral characteristics of *N-tert*-butyl-1,5,3-dithiazepinane (**1**) agree with the published data [16].

1-Oxa-3,6-dithiacycloheptane (2). A mixture of a 37% aqueous formalin solution (14.8 ml, 0.2 mol) and 1,2-ethanedithiol (8.3 ml, 0.1 mol) was stirred at 20°C for 3 h and extracted with $CHCl_3$. The extract was evaporated, and 1-oxa-3,6-dithiacycloheptane (**2**) was isolated. Yield 11.6 g (85%). Crystals, mp 42-44°C ($CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.98 (4H, br. s, 4,5-CH_2); 5.33 (4H, br. s, 2,7-CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 32.0 (C-4,5); 66.2 (C-2,7). Found, %: C 35.21; H 5.90; S 47.10. $C_4H_8OS_2$. Calculated, %: C 35.27; H 5.92; S 47.07.

Preparation of Compounds 3-11 (General Method). A. Transamination of *N-tert*-butyl-1,5,3-dithiazepinane (**1**) with aromatic amines: A mixture of *N-tert*-butyl-1,5,3-dithiazepinane (**1**) (0.191 g, 1 mmol, or 0.382 g, 2 mmol) (depending on the starting reagent molar ratio) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.022 g, 0.05 mmol) in $CHCl_3$ (5 ml) was stirred under an argon atmosphere at room temperature for 30 min, and the corresponding amine (1 mmol) in EtOH or $CHCl_3$ (5 ml) (depending on the solubility) was then added dropwise. The *p*-phenylenediamine was first activated with sulfur and NaOH by the method given in [18] in order to form the active complex. The reaction mixture was stirred at room temperature for 3 h. Then water (2 ml) was added, the mixture was stirred for 30 min and extracted with $CHCl_3$ (20 ml). The organic extract was evaporated, and the residue was chromatographed on a column of SiO_2.

B. Recyclization of 1-oxa-3,6-dithiacycloheptane (**2**) with aromatic amines. The reaction was conducted similarly to method A, using 1-oxa-3,6-dithiacycloheptane (**2**) (0.136 g, 1 mmol or 0.272 g, 2 mmol).

2-(1,5,3-Dithiazepinan-3-yl)phenol (3). Yield 0.12 g (51%, method A), 0.17 g (75%, method B). Crystals, mp 82-84°C ($CHCl_3$), R_f 0.9 (Sorbfil, PhMe–EtOAc–Me_2CO, 8:1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.08 (4H, br. s, 6',7'-CH_2); 4.55 (4H, br. s, 2',4'-CH_2); 6.76 (1H, br. s, OH); 6.88 (1H, dd, *J* = 8.0, *J* = 8.0, H-4); 6.97 (1H, d, *J* = 8.0, H-3); 7.14 (1H, dd, *J* = 8.0, *J* = 8.0, H-5); 7.52 (1H, d, *J* = 8.0, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 38.0 (C-6',7'); 59.3 (C-2',4'); 114.6 (C-3); 120.3 (C-4); 124.6 (C-6); 127.7 (C-5); 136.8 (C-2); 151.6 (C-1). Found, *m/z*: 228.386 $[M+H]^+$. $C_{10}H_{14}NOS_2$. Calculated, *m/z*: 228.348. Found, %: C 52.79; H 5.71; N 6.15; S 28.18. $C_{10}H_{13}NOS_2$. Calculated, %: C 52.83; H 5.76; N 6.16; S 28.21.

4-(1,5,3-Dithiazepinan-3-yl)phenol (4). Yield 0.14 g (60%, method A), 0.20 g (85%, method B). Crystals, mp 91-93°C ($CHCl_3$), R_f 0.8 (Sorbfil, PhMe–EtOAc–Me_2CO, 4:1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.08 (4H, br. s, 6',7'-CH_2); 4.73 (4H, br. s, 2',4'-CH_2); 5.04 (1H, br. s, OH); 6.81 (2H, d, *J* = 8.0, H-3,5); 6.89 (2H, d, *J* = 8.0, H-2,6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 36.0 (C-6',7'); 56.4 (C-2',4'); 116.1 (C-3,5); 118.7 (C-2,6); 140.5 (C-4); 149.8 (C-1). Found, *m/z*: 227.913 $[M]^+$. $C_{10}H_{13}NOS_2$. Calculated, *m/z*: 227.348. Found, %: C 52.80; H 5.73; N 6.14; S 28.20. $C_{10}H_{13}NOS_2$. Calculated, %: C 52.83; H 5.76; N 6.16; S 28.21.

4-(1,5,3-Dithiazepinan-3-yl)benzoic Acid (5). Yield 0.16 g (63%, method A), 0.20 g (76%, method B). Crystals, mp 240-242°C ($CHCl_3$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.07 (4H, br. s, 6',7'-CH_2); 4.86

(4H, br. s, 2',4'-CH_2); 6.98 (2H, d, *J* = 8.0, H-3,5); 7.81 (2H, d, *J* = 8.0, H-2,6); 12.34 (1H, br. s, COOH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 34.2 (C-6',7'); 53.3 (C-2',4'); 114.9 (C-3,5); 120.6 (C-1); 130.9 (C-2,6); 149.0 (C-4); 167.7 (COOH). Found, *m/z*: 255.909 $[M]^+$. $C_{11}H_{13}NO_2S_2$. Calculated, *m/z*: 255.358. Found, %: C 51.69; H 5.10; N 5.44; S 25.07. $C_{11}H_{13}NO_2S_2$. Calculated, %: C 51.74; H 5.13; N 5.49; S 25.11.

5-(1,5,3-Dithiazepinan-3-yl)-2-hydroxybenzoic Acid (6). Yield 0.15 g (57%, method A), 0.18 g (67%, method B). Crystals, mp 197-199°C ($CHCl_3$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.06 (4H, br. s, 6',7'-CH_2); 4.75 (4H, br. s, 2',4'-CH_2); 6.87 (1H, d, *J* = 8.0, H-4); 7.21-7.24 (1H, m, H-6); 7.29 (1H, d, *J* = 8.0, H-3). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 34.5 (C-6',7'); 54.9 (C-2',4'); 113.5 (C-1); 116.9 (C-4); 117.8 (C-3); 125.3 (C-6); 138.1 (C-5); 155.1 (C-2); 172.3 (COOH). Found, *m/z*: 271.218 $[M]^+$. $C_{11}H_{13}NO_3S_2$. Calculated, *m/z*: 271.357. Found, %: C 48.63; H 4.77; N 5.11; S 23.65. $C_{11}H_{13}NO_3S_2$. Calculated, %: C 48.69; H 4.83; N 5.16; S 23.63.

4-(1,5,3-Dithiazepinan-3-yl)thiophenol (7). Yield 0.11 g (45%, method A), 0.18 g (74%, method B). Crystals, mp >197°C (decomp., $CHCl_3$), R_f 0.8 (Sorbfil, PhMe–EtOAc–Me_2CO, 8:1:1), ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.76 (1H, br. s, SH); 3.06 (4H, br. s, 6',7'-CH_2); 4.76 (4H, br. s, 2',4'-CH_2); 6.84 (2H, d, *J* = 8.8, H-3,5); 7.43 (2H, d, *J* = 8.8, H-2,6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 37.7 (C-6',7'); 54.4 (C-2',4'); 116.2 (C-3,5); 128.2 (C-4); 132.0 (C-2,6); 145.8 (C-1). Found, *m/z*: 242.332 $[M-H]^+$. $C_{10}H_{12}NS_3$. Calculated, *m/z*: 242.415. Found, %: C 49.30; H 5.35; N 5.71; S 39.55. $C_{10}H_{13}NS_3$. Calculated, %: C 49.34; H 5.38; N 5.75; S 39.52.

1,3,6,8-Benzotrithiazecinane (8). Yield 0.12 g (48%, method A), 0.16 g (62%, method B). Oil, n_D^{20} 1.5145, R_f 0.9 (Sorbfil, $CHCl_3$–hexane, 5:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.84 (4H, br. s, 4,5-CH_2); 4.44 (2H, br. s, 2-CH_2); 4.82 (2H, br. s, 7-CH_2); 6.49 (1H, d, *J* = 8.0, H-9); 6.74 (1H, t, *J* = 7.4, H-10); 6.98 (1H, t, *J* = 7.6, H-11); 7.08 (1H, d, *J* = 7.2, H-12). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 32.4 (C-4,5); 52.3 (C-2); 55.7 (C-7); 108.7 (C-9); 120.3 (C-11); 122.5 (C-10); 125.6 (C-12); 127.7 (C-12a); 145.7 (C-8a). Found, *m/z*: 283.265 $[M+K+H]^+$. $C_{10}H_{14}KNS_3$. Calculated, *m/z*: 283.415. Found, %: C 49.30; H 5.33; N 5.72; S 39.57. $C_{10}H_{13}NS_3$. Calculated, %: C 49.34; H 5.38; N 5.75; S 39.52.

3,3'-(1,2-Phenylene)bis-1,5,3-dithiazepinane (9). Yield 0.15 g (43%, method A), 0.23 g (65%, method B). Crystals, 210-212°C ($CHCl_3$), R_f 0.9 (Sorbfil, C_6H_6–EtOH, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.08 (8H, br. s, 6',6",7',7"-CH_2); 4.78 (8H, br. s, 2',2",4',4"-CH_2); 7.05-7.07 (2H, m, H-3,6); 7.19-7.22 (2H, m, H-4,5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 37.3 (C-6',6",7',7"); 56.6 (C-2',2",4',4"); 122.1 (C-4,5); 124.0 (C-3,6); 142.1 (C-1,2). Found, *m/z*: 345.227 $[M+H]^+$. $C_{14}H_{21}N_2S_4$. Calculated, *m/z*: 345.586. Found, %: C 48.77; H 5.80; N 8.09; S 37.20. $C_{14}H_{20}N_2S_4$. Calculated, %: C 48.80; H 5.85; N 8.13; S 37.22.

3,3'-(1,4-Phenylene)bis-1,5,3-dithiazepinane (10). Yield 0.16 g (45%, method A), 0.23 g (66%, method B). Crystals, mp 235-236°C ($CHCl_3$), R_f 0.85 (Sorbfil, C_6H_6–EtOH, 9:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.07 (8H, br. s, 6',6",7',7"-CH_2); 4.74 (8H, br. s, 2',2",4',4"-CH_2); 7.36 (4H, br. s, H-2,3,5,6). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 34.5 (C-6',6",7',7"); 54.7 (C-2',2",4',4"); 116.8 (C-2,3,5,6); 141.1 (C-1,4). Found, *m/z*: 344.269 $[M]^+$. $C_{14}H_{20}N_2S_4$. Calculated, *m/z*: M 344.586. Found, %: C 48.79; H 5.82; N 8.11; S 37.23. $C_{14}H_{20}N_2S_4$. Calculated, %: C 48.80; H 5.85; N 8.13; S 37.22.

3,3'-[Methylenebis(1,4-phenylene)]bis-1,5,3-dithiazepinane (11). Yield 0.23 g (52%, method A), 0.30 g (67%, method B). Crystals, mp 145-147°C ($CHCl_3$), R_f 0.80 (Sorbfil, C_6H_6–EtOH, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.07 (8H, br. s, 6",6'",7",7'"-CH_2); 3.87 (2H, br. s, Ar$\underline{C}H_2$Ar); 4.77 (8H, br. s, 2",2'",4",4'"-CH_2); 6.87 (4H, d, *J* = 8.8, H-2,2',6,6'); 7.14 (4H, d, *J* = 8.8, H-3,3',5,5'). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.8 (C-6",6'",7",7'"); 40.1 (Ar$\underline{C}H_2$Ar); 55.2 (C-2",2'",4",4'"); 116.1 (C-2,2',6,6'); 129.6 (C-3,3',5,5'); 133.1 (C-4,4'); 144.0 (C-1,1'). Found, *m/z*: 457.172 $[M+Na]^+$. $C_{21}H_{26}N_2S_4Na$. Calculated, *m/z*: 457.708. Found, %: C 57.95; H 5.98; N 6.38; S 29.57. $C_{21}H_{26}N_2S_4$. Calculated, %: C 58.02; H 6.03; N 6.44; S 29.50.

1-Oxa-3,7-dithiacyclooctane (12). A 37% formalin solution (14.8 ml, 0.2 mol) and 1,3-propanedithiol (10 ml, 0.1 mol) were placed in a round-bottom flask fitted with a stirrer. The mixture was stirred at 20°C for 3 h. The reaction mixture was extracted with $CHCl_3$, and the extract was evaporated. Yield 8.4 g (55%). Oil,

n_D^{20} 1.5715. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.88 (2H, br. s, 5-CH_2); 2.60 (4H, br. s, 4,6-CH_2); 4.59 (4H, br. s, 2,8-CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 29.3 (C-5); 29.9 (C-4,6); 79.8 (C-2,8). Found, %: C 39.92; H 6.68; S 42.72. $C_5H_{10}OS_2$. Calculated, %: C 39.97; H 6.71; S 42.68.

1,5,3-Dithiazocinanes 13-17 (**General Method)**. Depending on the molar ratio of the starting reagents, 1-oxa-3,7-dithiacyclooctane (**12**) (0.15 g, 1 mmol or 0.30 g, 3 mmol) in $CHCl_3$ (5 ml) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.022 g, 0.05 mmol) were placed in a Schlenk flask on a magnetic stirrer. The mixture was stirred at ~20°C for 30 min, and the corresponding arylamine (1 mmol) in EtOH or $CHCl_3$ (5 ml) (depending on solubility) was then added dropwise. The reaction mixture was stirred at ~20°C for 3 h, and H_2O (2 ml) was added. The mixture was stirred for 30 min and extracted with $CHCl_3$ (20 ml). The chloroform fractions were chromatographed on columns with SiO_2.

2-(1,5,3-Dithiazocinan-3-yl)phenol (13). Yield 0.15 g (61%). Oil, n_D^{20} 1.5673, R_f 0.80 (Sorbfil, $CHCl_3$–EtOAc–hexane, 1:5:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.75-1.78 (2H, m, 7'-CH_2); 2.54-2.58 (4H, m, 6',8'-CH_2); 4.32-4.37 (4H, m, 2',4'-CH_2); 6.42 (1H, br. s, OH); 6.88 (1H, dd, *J* = 8.0, *J* = 8.0, H-4); 6.96 (1H, d, *J* = 8.0, H-3); 7.11 (1H, d, *J* = 8.0, H-6); 7.22 (1H, dd, *J* = 8.0, *J* = 8.0, H-5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 29.4 (C-7'); 30.7 (C-6',8'); 55.9 (C-2',4'); 115.0 (C-4); 120.3 (C-3); 125.2 (C-5); 127.4 (C-6); 135.4 (C-2); 151.3 (C-1). Found, *m/z*: 242.362 $[M+H]^+$. $C_{11}H_{16}NOS_2$. Calculated, *m/z*: 242.374. Found, %: C 54.68; H 6.21; N 5.76; S 26.60. $C_{11}H_{15}NOS_2$. Calculated, %: C 54.74; H 6.26; N 5.80; S 26.57.

4-(1,5,3-Dithiazocinan-3-yl)phenol (14). Yield 0.16 g (68%). Oil, n_D^{20} 1.6037, R_f 0.85 (Sorbfil, PhMe–EtOAc–Me_2CO, 4:1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.79-1.83 (2H, m, 7'-CH_2); 2.72 (4H, t, *J* = 5.8, 6',8'-CH_2); 4.50 (1H, br. s, OH); 4.76 (4H, br. s, 2',4'-CH_2); 6.80-6.85 (4H, m, H-2,3,5,6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 28.9 (C-6',8'); 32.2 (C-7'); 57.0 (C-2',4'); 114.5 (C-3,5); 116.2 (C-2,6); 137.4 (C-4); 148.4 (C-1). Found, *m/z*: 242.351 $[M+H]^+$. $C_{11}H_{16}NOS_2$. Calculated, *m/z*: 242.374. Found, %: C 54.70; H 6.21; N 5.78; S 26.59. $C_{11}H_{15}NOS_2$. Calculated, %: C 54.74; H 6.26; N 5.80; S 26.57.

4-(1,5,3-Dithiazocinan-3-yl)thiophenol (15). Yield 0.22 g (83%). Crystals, mp 273-274°C ($CHCl_3$), R_f 0.8 (Sorbfil, PhMe–EtOAc–Me_2CO, 8:1:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.66-1.69 (2H, m, 7'-CH_2); 2.62 (4H, t, *J* = 5.8, 6',8'-CH_2); 4.85 (4H, br. s, 2',4'-CH_2); 6.89 (2H, d, *J* = 8.8, H-3,5); 7.37 (2H, d, *J* = 8.8, H-2,6). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 28.4 (C-6',8'); 32.40 (C-7'); 55.6 (C-2',4'); 114.7 (C-3,5); 124.6 (C-4); 132.7 (C-2,6); 144.4 (C-1). Found, *m/z*: 256.251 $[M-H]^+$. $C_{11}H_{14}NS_3$. Calculated, *m/z*: 256.441. Found, %: C 51.28; H 5.82; N 5.41; S 37.40. $C_{11}H_{15}NS_3$. Calculated, %: C 51.32; H 5.87; N 5.44; S 37.36.

4-(1,5,3-Dithiazocinan-3-yl)benzoic Acid (16). Yield 0.21 g (76%). Crystals, mp 202-204°C ($CHCl_3$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.67-1.69 (2H, m, 7'-CH_2); 2.63 (4H, t, *J* = 5.8, 6',8'-CH_2); 4.89 (4H, br. s, 2',4'-CH_2); 6.90 (2H, d, *J* = 8.8, H-3,5); 7.80 (2H, d, *J* = 8.8, H-2,6); 12.25 (1H, br. s, COOH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 27.9 (C-6',8'); 31.8 (C-7'); 55.0 (C-2',4'); 112.9 (C-3,5); 119.8 (C-1); 130.5 (C-2,6); 147.1 (C-4); 167.3 (COOH). Found, *m/z*: 270.250 $[M+H]^+$. $C_{12}H_{16}NO_2S_2$. Calculated, *m/z*: 270.385. Found, %: C 53.47; H 5.56; N 5.18; S 23.86. $C_{12}H_{15}NO_2S_2$. Calculated, %: C 53.50; H 5.61; N 5.20; S 23.81.

3,3'-[Methylenebis(1,4-phenylene)]bis-1,5,3-dithiazocinane (17). Yield 0.32 g (68%). Crystals, mp 175-176°C ($CHCl_3$), R_f 0.9 (Sorbfil, PhMe–EtOAc–Me_2CO, 8:1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.77-1.83 (4H, m, 7",7'"-CH_2); 2.72 (8H, t, *J* = 5.8, 6",6'",8",8'"-CH_2); 3.88 (2H, br. s, Ar$C\underline{H}_2$Ar); 4.76 (8H, br. s, 2",2'",4",4'"-CH_2); 6.85 (4H, d, *J* = 8.4, H-2,2',6,6'); 7.16 (4H, d, *J* = 8.4, H-3,3',5,5'). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 28.9 (C-6",6'",8",8'"); 32.1 (C-7",7'"); 40.0 (Ar$\underline{C}H_2$Ar); 56.7 (C-2",2'",4",4'"); 113.3 (C-2,2',6,6'); 129.7 (C-3,3',5,5'); 132.0 (C-4,4'); 141.4 (C-1,1'). Found, *m/z*: 463.175 $[M+H]^+$. $C_{23}H_{31}N_2S_4$. Calculated, *m/z*: 463.761. Found, %: C 59.65; H 6.49; N 5.96; S 27.79. $C_{23}H_{30}N_2S_4$. Calculated, %: C 59.70; H 6.53; N 6.05; S 27.72.

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