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Synthesis of dithiaza- and dioxadithiazacycloalkanes by cyclothiomethylation of arylamines with formaldehyde and α,ω-dithiols

Guzel R. Khabibullina[1]*, Ekaterina S. Fedotova[1], Ekaterina S. Meshcheryakova[1], Tatyana M. Buslaeva[2], Vnira R. Akhmetova[1], Askhat G. Ibragimov[1]

[1] *Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 Oktyabrya Ave., Ufa 450075, Russia; e-mail: khabibguzel@gmail.com*

[2] *M. V. Lomonosov Institute of Fine Chemical Technologies, Moscow Technological University, 78 Vernadskogo Ave., Moscow 119454, Russia; e-mail: buslaevatm@mail.ru*

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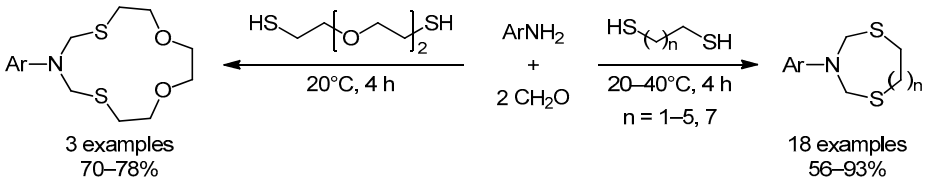


New derivatives of 1,5,3-dithiazepanes and macroheterocycles were synthesized by a three-component cyclothiomethylation of arylamines with formaldehyde and α,ω-dithiols. The sorption properties of 3-phenyl-1,5,3-dithiazepane and 6-phenyl-1,11-dioxa-4,8-dithia-6-azacyclotridecane applicable for the extraction of Ag(I) and Pd(II) ions from nitric acid solutions at room temperature were studied by a static method.

Keywords: arylamines, 1,5,3-dithiazepanes, catalysis, cyclothiomethylation, macroheterocycles, multicomponent reaction, sorption of silver(I) and palladium(II).

Multicomponent[1,2] and domino reactions[3] are widely used as tools of organic synthesis, since they are compatible with the main principles of green chemistry,[4] allowing to decrease the number of technological steps and to reduce waste.

An example of multicomponent reactions is the cyclothiomethylation of amines with formaldehyde and H_2S in water,[5,6] enabling the construction of 1,3,5-dithiazinanes,[7] 1,3,5-thiadiazinanes,[8] and in the case of bifunctional amines also fused and macrocyclic heterocycles.[9,10] Some of the heterocycles obtained by the aforementioned methods have exhibited antifungal[11] and anti-inflammatory activity,[12] are used as pharmaceuticals,[13] insecticides (buprofezin), herbicides, and bactericides. Besides that, such compounds are used as transition metal complexes.[14]

Dithiazacycloalkanes, in particular 1,5,3-dithiazinanes and 1,5,3-dithiazepanes, have a strong affinity for binding iridium(III), iridium(IV),[15] platinum(II), platinum(IV),[16] and palladium(II)[17] ions from hydrochloric acid and chloride solutions, as well as silver(I) and mercury(II) from nitric acid solutions.[18]

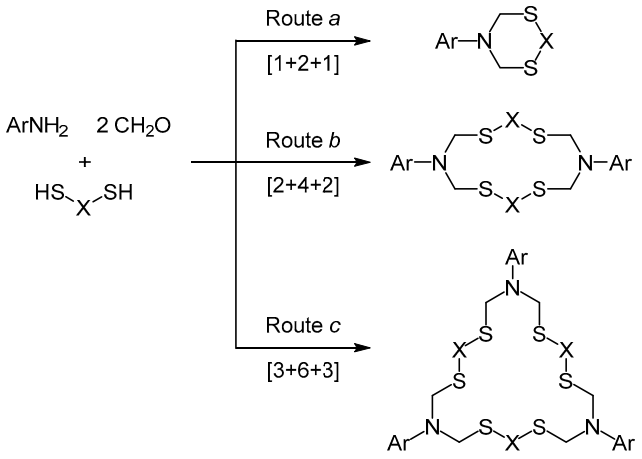
The objective of this work was to synthesize new derivatives of dithiaza- and dioxadithiazacycloalkanes by multicomponent cyclothiomethylation reactions of arylamines with formaldehyde and α,ω-dithiols, to study the reactivity trends in these processes and to determine the sorption ability of the obtained compounds.

It was recently shown for the case of amino alcohols[19] and carboxylic acid hydrazides[20] that, depending on the structure of the starting α,ω-dithiols, the three-component cyclothiomethylation followed the scheme of [n+2n+n] cyclocondensation. The reaction of anilines with 1,2-ethane- and 1,3-propanedithiols in the presence of Sm and Co complexes proceeded as a [1+2+1] cyclocondensation.[21]

In order to expand the range of applicability of these reactions and to synthesize new types of dithiazacycloalkanes, we studied the reaction of arylamines with formaldehyde and α,ω-dithiols. This reaction can proceed by several routes (Scheme 1): route *a* – intermolecular cyclocondensation of amines with the formation of two C–N bonds and two C–S bonds involving one molecule of amine, two molecules of CH_2O, and one molecule of dithiol according to a [1+2+1] scheme; route *b* – intermolecular

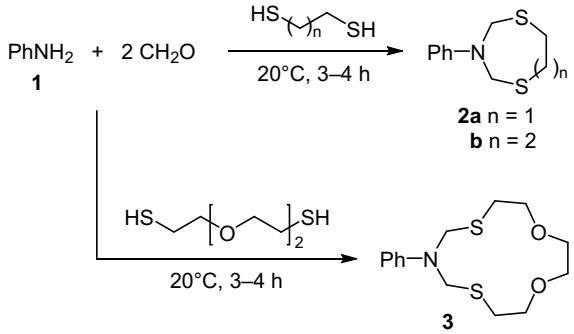
[2+4+2] cyclocondensation of two amine molecules, four CH_2O molecules, and two dithiol molecules forming heterochain-containing N,S-macroheterocycles; route *c* – intermolecular [3+6+3] cyclocondensation.

Scheme 1



Cyclothiomethylation of aniline (**1**) with formaldehyde and 1,2-ethanedithiol in 1:2:1 molar ratio of the starting materials and ~20°C temperature without using solvents was complete in 3 h and gave 3-phenyl-1,5,3-dithiazepane (**2a**) in 77% yield (Scheme 2). 1,3-Propanedithiol and 3,6-dioxa-1,8-octanedithiol participated in a multicomponent reaction with aniline (**1**) and CH_2O under analogous solvent-free conditions, forming 3-phenyl-1,5,3-dithiazocane (**2b**) and 6-phenyl-1,11-dioxa-4,8-dithia-6-azacyclotridecane (**3**) in 73 and 70% yields, respectively. Thus, the multicomponent cyclothiomethylation of aniline (**1**) with formaldehyde and 1,2-ethane-, 1,3-propanedithiol, or 3,6-dioxa-1,8-octanedithiol under solvent-free conditions followed the route *a* with the formation of [1+2+1] cyclocondensation products. It should be added that, in contrast to arylamines, amino alcohols reacted with CH_2O and 1,3-propane- or 1,4-butanedithiol according to route *b*, but with 4,4'-dimercaptodiphenyloxide – by route *c*.[19]

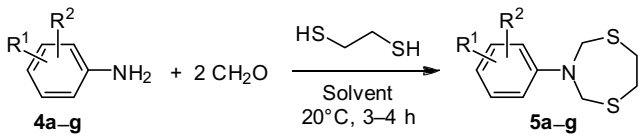
Scheme 2



The developed one-pot synthesis allowed to obtain dithiazacycloalkanes **2a**,**b**, **3** in sufficiently high yields without using solvents and catalysts, which is desirable according to the principles of green chemistry. Furthermore, the only by-product in this reaction was water.

Nitro derivatives of benzocrown ethers are known to exhibit high selectivity for the extraction of palladium(II) ions from hydrochloric acid solutions.[22] Based on these data, as well as in order to extend the practical applicability of dithiazacycloalkanes, the synthesis of dithiazacycloalkane nitro derivatives was performed with various functional substituents in the aromatic ring. It was experimentally established that the nitro-substituted arylamines **4a**–**g** readily underwent intermolecular [1+2+1] cyclocondensation with CH_2O and 1,2-ethanedithiol, forming 1,5,3-dithiazepanes **5a**–**g** in 74–93% yields (Scheme 3). Taking into account the solubility of the starting arylamines, the synthesis of compounds **5a**–**e** was performed in ethyl acetate, compound **5f** – in chloroform, and compound **5g** – in acetone.

Scheme 3



4, **5 a** R^1 = H, R^2 = 2-NO_2 (86%); **b** R^1 = H, R^2 = 3-NO_2 (78%); **c** R^1 = H, R^2 = 4-NO_2 (85%); **d** R^1 = 4-Me, R^2 = 3-NO_2 (85%); **e** R^1 = 2-Me, R^2 = 3-NO_2 (74%); **f** R^1 = 4-F, R^2 = 3-NO_2 (93%); **g** R^1 = 4-OH, R^2 = 3-NO_2 (86%)

^{1}H NMR spectra of *N*-aryl-1,5,3-dithiazepanes **5b**–**g** featured signals of NCH_2S and SCH_2CH_2 protons as narrow singlets. A non-equivalence of geminal methylene protons located between the N and S atoms of dithiazepane rings was observed in compound **5a**, probably due to the influence of nitro group present at the *ortho* position, while the NCH_2S protons were observed as two singlets at 4.58 and 4.60 ppm.

Monocrystals of dithiazacycloalkanes **2a**,**b** and **5d**,**g** were obtained, and their structure was confirmed by X-ray structural analysis (Fig. 1).

According to the data of X-ray structural analysis, 1,5,3-dithiazepane ring of compound **2a** assumed a "twist-boat" conformation in the crystal structure, while in compound **5d** this ring had a "twist" conformation, and in compound **5g** it had a "boat" conformation with the S(1) and S(2) sulfur atoms deviating from ring plane by –0.864(4) and –0.788(3) Å, respectively. The 1,5,3-dithiazocane ring in compound **2b** assumed a "twist-chair" conformation. It should be noted that the *N*-aryl substituent in dithiazacycloalkanes **2a**,**b** and **5d**,**g** was axially oriented relative to the plane of heterocyclic moiety, while in compounds **2a**,**b** the angle between the average planes of these rings was equal to 63.835(6) and 69.019(6)°, respectively. An intramolecular hydrogen bond between the hydroxy group proton and the oxygen atom of aromatic nitro group occurred in compound **5g**, with the O–H···O distance equal to 1.992(5) Å.

In order to synthesize dithiazacycloalkanes **6a**–**e**, **7a**–**d** containing heterocycles of various sizes, aliphatic α,ω-di-

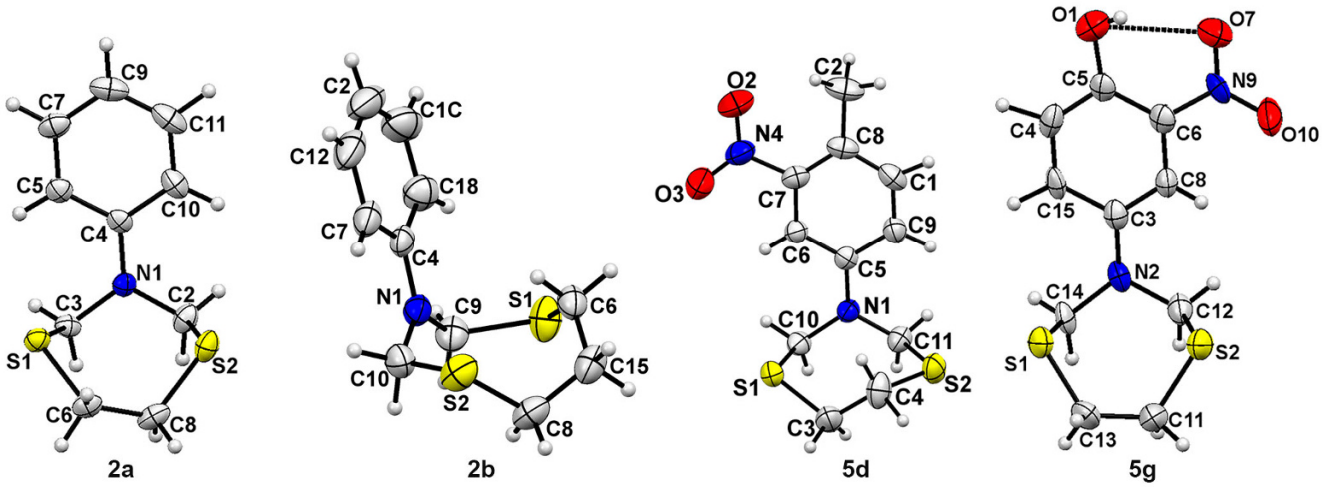
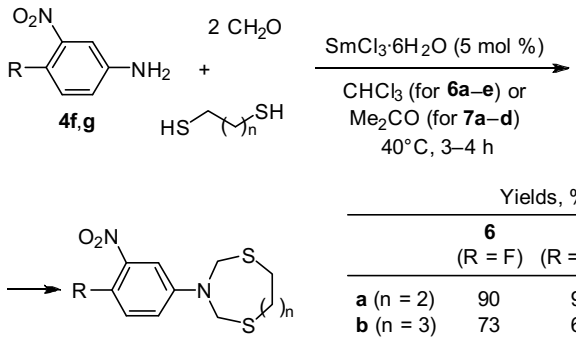


Figure 1. Molecular structures of compounds **2a**,**b** and **5d**,**g** according to data of X-ray structural analysis, with atoms represented by thermal vibration ellipsoids of 50% probability.

thiols (1,3-propane-, 1,4-butane-, 1,5-pentane-, 1,6-hexane-, and 1,8-octanedithiols) were used in reactions with nitroanilines **4f**,**g** and CH_2O.

It was found that the reactions with nitroaniline **4f** under the conditions described above ($CHCl_3$, 20°C) gave dithiazacycloalkanes **6a**–**e** in yields that decreased from 73 to 24% upon increasing the alkyl chain length in the starting α,ω-dithiols. A higher yield of the necessary macroheterocyclic compounds could be obtained by performing the reactions of nitroanilines **4f**,**g** with α,ω-dithiols in the presence of $SmCl_3 \cdot 6H_2O$ catalyst at 40°C (Scheme 4). Our proposed reaction conditions allowed to obtain the dithiazacycloalkanes **6a**–**e** and **7a**–**d** in 56–91% yields. The use of other catalysts ($Sm(NO_3)_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$) under the same conditions gave the target compounds **6a**–**e**, **7a**–**d** in 50–68% yields.

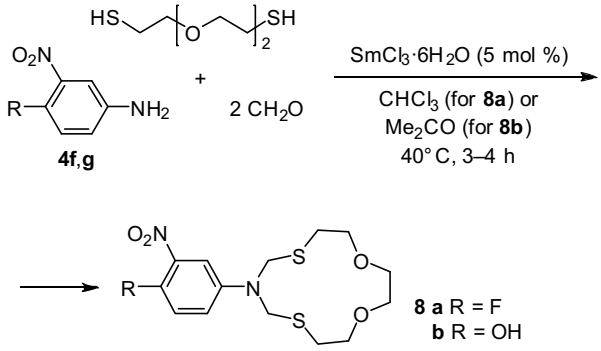
Scheme 4



	Yields, %	
	6 (R = F)	**7** (R = OH)
a (n = 2)	90	91
b (n = 3)	73	67
c (n = 4)	76	57
d (n = 5)	71	67
e (n = 7)	56	–

The cyclothiomethylation reaction of arylamines **4f**,**g** with CH_2O and 3,6-dioxa-1,8-octanedithiol in the presence of $SmCl_3 \cdot 6H_2O$ as catalyst enabled the synthesis of new macroheterocycles **8a**,**b** (Scheme 5). Cyclothiomethylation of nitroanilines **4f**,**g** was performed depending on the solubility of the starting compounds either in chloroform or acetone at 40°C, giving the target compounds **8a**,**b** in 74 and 78% yields.

Scheme 5



The structure of compounds **8a**,**b** was proved by spectral methods. The protons of NCH_2S methylene groups in compounds **3** and **8a**,**b** gave ^1H NMR signals as singlets in the upfield region at 5.07–5.13 ppm. A characteristic ^1H NMR feature for all compounds **3**, **8a**,**b** was the appearance of SCH_2CH_2O methylene group protons at 2.66–2.70 and 3.89–3.92 ppm, respectively, as triplets with J_{HH} = 4.5 or 4.6 Hz, and the OCH_2CH_2O protons as a singlet at 3.68–3.72 ppm.

Besides that, monocrystals were obtained for compounds **3** and **8b** and X-ray structural analysis was performed (Fig. 2). It was shown that the 1,11-dioxa-4,8-dithia-6-azacyclotridecane moiety of compound **3** had a "chair-twist-chair" conformation, while in compound **8b** it had a "boat-twist-chair" conformation. The *N*-aryl substituents in molecules of compounds **3**, **8b** occupied an equatorial position relative to the planes of heterocyclic moieties. The average ring planes in compounds **3**, **8b** formed angles of 21.689(7)° and 51.804(6)°, respectively. The structure of compound **8b** featured an intramolecular O–H···O hydrogen bond, the length of which was 1.799(12) Å. However, despite the substantial differences of geometry between the considered compounds, their crystals belonged to the same monoclinic lattice type with $P2_1/c$ space group.

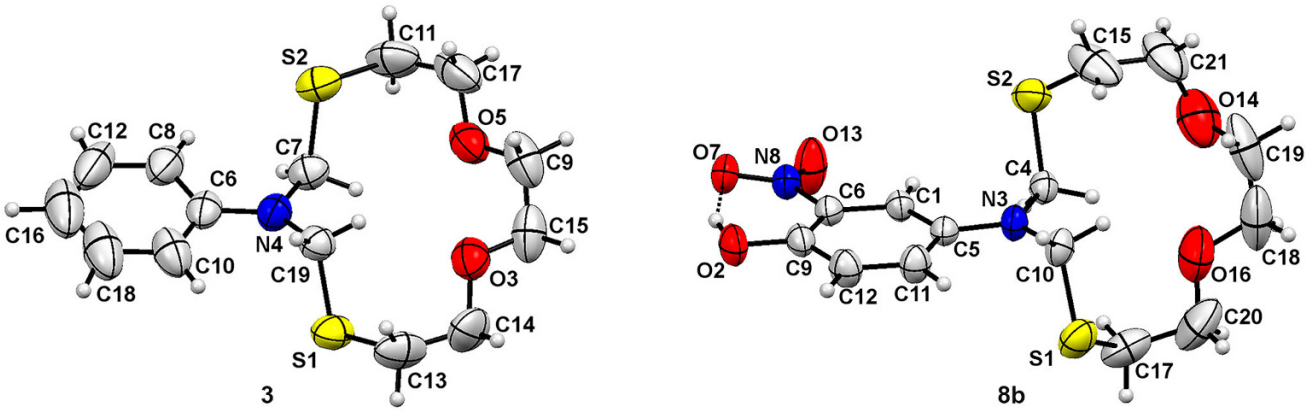


Figure 2. The molecular structures of compounds **3** and **8b** according to X-ray structural analysis data, with atoms represented by thermal vibration ellipsoids of 50% probability.

Considering that palladium(II) ions serve as a soft Lewis acid according to the Pearson concept and form stable complexes with S- and S,N-containing molecules, we estimated the sorption ability of dithiazacycloalkanes **2a** and **3** with respect to Pd(II) and Ag(I) ions in 0.1–4.0 M HNO_3 solutions under static conditions. At HNO_3 concentrations of less than 0.1 M palladium(II) nitrates are not stable,[23] but changing the acid concentration in the range of 0.1–2.0 M did not substantially affect the extent of palladium(II) extraction. Increasing the HNO_3 concentration to 4.0 M resulted in a lower sorption capacity. The starting concentration of metal ions was varied in the range from $4\cdot10^{-4}$ to $1.3\cdot10^{-2}$ mol/l. It should be noted that when the Pd(II) ion concentration in the solution was changed to 10^{-3} mol/l, the degree of extraction by compounds **2a** and **3** was 100 and 72%, while the sorption capacity was 0.48 and 0.34 mmol/g, respectively. At Pd(II) ion concentration of 10^{-2} mol/l the values of sorption capacity were 1.76 mmol/g for compound **2a** and 1.37 mmol/g for compound **3**.

The difficulty of Pd(II) ion desorption from the sorbent phase upon treatment with 14% aqueous ammonia and 5% solution of thiourea in 0.1 M HCl indirectly confirmed that the sorption process partially involved the formation of coordination complexes with nitrogen. The sorption capacity for Ag(I) ions (10^{-2} mol/l in 0.1 M HNO_3) was equal to 7.40 mmol/g for compound **2a** and 3.93 mmol/g for compound **3**, which was lower than in the case of bisheterocyclic compounds.[17,18]

Thus, the three-component cyclothiomethylation of arylamines with formaldehyde and aliphatic α,ω-dithiols occurred as a [1+2+1] cyclocondensation. Aniline reacted with CH_2O and 1,2-ethane-, 1,3-propanedithiols, as well as with 3,6-dioxa-1,8-octanedithiol under solvent-free conditions in the absence of a catalyst, giving high yields of *N*-phenyl-substituted 1,5,3-dithiazepane, 1,5,3-dithiazocane, and 6-phenyl-1,11-dioxa-4,8-dithia-6-azacyclotridecane. The reaction of substituted anilines with CH_2O and 1,2-ethanedithiol at 20°C provided 1,5,3-dithiazepanes, while α,ω-dithiols (1,3-propane-, 1,4-butane-, 1,5-pentane-, 1,6-hexane-, 1,8-octanedithiols and 3,6-dioxa-1,8-octanedithiol) formed dithiazacycloalkanes and dioxadithiazacyclotridecane in the presence of $SmCl_3\cdot6H_2O$ as a catalyst. Analysis by IR and electronic spectroscopy allowed to establish that the sorption process from nitric acid solutions involved complex formation between the palladium ions and molecules of saturated bicyclic S,N-containing heterocycles, forming metal–nitrogen bonds. It was shown that the sorption of Pd(II) and Ag(I) ions from aqueous nitric acid solutions occurred irreversibly, thus the use of 3-phenyl-1,5,3-dithiazepane and 6-phenyl-1,11-dioxa-4,8-dithia-6-azacyclotridecane for the concentration of Pd(II) and Ag(I) ions is of practical value only for analytical purposes.

Experimental

IR spectra were recorded on a Bruker Vertex 70v spectrometer. The spectra of oily products (compounds **5e**, **6b**–**e**, **7b**–**d**) were recorded for thin films, the spectra of powders (the rest of the compounds except **5c**) – in KBr pellets, the spectrum of compound **5c** – in a Nujol mull. UV spectra were recorded on a Perkin Elmer Lambda 750 UV/Vis spectrometer in $CHCl_3$ over the wavelength range of 200–1000 nm, cuvette thickness 0.2 cm. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Ascend 500 spectrometer (500 and 125 MHz, respectively, compounds **2a**, **3**, **5a**) and Bruker Avance 400 spectrometer (400 and 100 MHz, respectively, the rest of the compounds). Homonuclear (NOESY, ^{1}H–^{1}H COSY) and heteronuclear (^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC) 2D NMR spectra of compounds **5f**,**g**, **6a**,**c**, **7b**, **8a**,**b** were acquired on a Bruker Ascend 500 spectrometer (500 MHz for ^{1}H nuclei, 125 MHz for ^{13}C nuclei). The solvents were DMSO-d_6 (compounds **5b**,**g**) and $CDCl_3$ (the rest of the compounds). Solvent signals were used as internal standard (DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei; $CDCl_3$: 7.28 ppm for ^{1}H nuclei, 77.1 ppm for ^{13}C nuclei). ^{19}F NMR spectra (470 MHz) were acquired on a Bruker Avance 500 spectrometer in $CDCl_3$, with $CFCl_3$ as internal standard. Mass spectra in MALDI-TOF mode were recorded on a Bruker Autoflex III MALDI-TOF spectrometer, using α-cyano-4-hydroxycinnamic and 2,5-dihydrobenzoic acid matrices, the sample was prepared by dried-droplet method with chloroform (1:10). The mass spectrum of compound **3** in

electrospray ionization mode was recorded on a Shimadzu LCMS-2010 EV liquid chromato-mass spectrometer (sample introduction by syringe, 0.1 ml/min, eluent MeCN–H_2O, 75:25) in positive and negative ion recording modes at capillary potentials of 4.5 and –3.5 kV, respectively. The interface capillary temperature was 250°C, the voltage on the interface capillary was 25 ÷ –25 V. The nebulizer gas (N_2) flow was 1.5 l/min. The high-frequency lenses (Q-array) voltage was 5 ÷ –5 V. The elemental composition of C, H, and N was determined on a Carlo Erba 1106 elemental analyzer. The sulfur content was determined by the Schoeniger method.[24] Melting points were determined with a RNMK 80/2617 apparatus (Kofler bench). The analysis of reaction products by gas-liquid chromatography was performed on a Chrom-5 chromatograph with flame ionization detector, with SE-30 (5%) stationary phase on Chromaton N-AW-HMDS support (2400 × 3 mm packed steel column, temperature program 50–270°C, 8°C/min, helium as carrier gas). The GC–MS analysis of compounds **5c**,**d** was performed on a Shimadzu GC 2010 gas chromatograph with GCMS-QP2010 Ultra mass spectral detector (Shimadzu, Japan) with Supelco 5ms capillary column (60 m × 0.25 mm × 0.25 μm), helium as carrier gas. The injector and interface temperatures were 260°C, the ion source temperature was 200°C. The ionization method was by electron impact at 70 eV. Individual compounds were isolated by chromatography on KSK silica gel (50–160 μm). The eluent used for column chromatography is indicated in the descriptions of the obtained compounds next to the R_f values. Analysis by TLC was performed on Silufol W-254 plates, visualization with iodine vapor. The concentration of palladium(II) in aqueous solutions was determined by spectrophotometric method with tin(II) chloride on a KFK-3-01 spectrophotometric colorimeter according to a published procedure,[26] the concentration of silver(I) was determined titrimetrically, using Volhard method.[27]

The starting arylamines and α,ω-dithiols with ≥98% assay and aqueous formaldehyde (37% formalin) were purchased from Acros and used without additional purification. Aqueous palladium(II) and silver(I) solutions were prepared from $Pd(NO_3)_2·2H_2O$ that was synthesized by a published procedure,[25] $AgNO_3$ of chemically pure grade (GOST 1277-76, produced by PZCM-Vtormet, Russia) and HNO_3 of chemically pure grade.

IR absorption spectra for solid complexes of compounds **2a** and **3** with Pd(II) or Ag(I) ions were recorded for KBr pellets on a Bruker Eq.55 FT-IR spectrometer over the range of 200–4000 cm^{-1}. The electronic absorption spectra for solutions containing complexes of compounds **2a** and **3** with Pd(II) or Ag(I) ions were recorded on a Specord Helios UV-Visible spectrophotometer over the wavelength range of 200–800 nm, cuvette thickness 1 cm. The diffuse reflectance spectra (DRS) for solid samples of complexes formed by compounds **2a** and **3** with Pd(II) or Ag(I) ions were recorded on a Specord M-40 spectrometer.

Cyclothiomethylation of aniline (1) (General method). A mixture of 1,2-ethanedithiol, 1,3-propanedithiol, or 3,6-dioxa-1,8-octanedithiol (1 mmol) and 37% formalin (0.15 ml, 2 mmol) was stirred for 30 min at room temperature. Aniline (**1**) (0.09 ml, 1 mmol) was then added dropwise and the mixture was stirred at room temperature for 3–4 h. The product was evaporated on a rotary evaporator and purified by column chromatography.

3-Phenyl-1,5,3-dithiazepane (2a).[21a] Yield 0.17 g (77%), colorless crystals, mp 42–44°C (hexane–$CHCl_3$, 1:2), R_f 0.78 (hexane–$CHCl_3$, 1:2). UV spectrum, λ_{max}, nm: 259.86. ^1H and ^{13}C NMR spectra were analogous to those reported in the literature.[21a]

3-Phenyl-1,5,3-dithiazocane (2b).[21a] Yield 0.16 g (73%), colorless crystals, mp 83–85°C (PhH–$CHCl_3$, 1:1), R_f 0.80 (PhH–$CHCl_3$, 1:1). ^1H and ^{13}C NMR spectra were analogous to those reported in the literature.[21a] Found, *m/z*: 226.476 $[M+H]^+$. $C_{11}H_{16}NS_2$. Calculated, *m/z*: 226.072.

6-Phenyl-1,11-dioxa-4,8-dithia-6-azacyclotridecane (3). Yield 0.21 g (70%), colorless crystals, mp 102–104°C (*cyclo*-C_6H_{12}–CH_2Cl_2, 1:1), R_f 0.48 (*cyclo*-C_6H_{12}–CH_2Cl_2, 1:1). UV spectrum, λ_{max}, nm: 261.07. IR spectrum, ν, cm^{-1}: 695 (C–S), 755 (C–S–C), 1071 (C–O–C), 1113 (C–N), 1142 (C–O–C), 1205 (C–N), 1270 (C–O–C), 2854 (CH_2), 2889 (C–H), 2922 (CH_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.70 (4H, t, *J* = 4.5, $2SC\underline{H}_2CH_2O$); 3.72 (4H, s, $O(C\underline{H}_2)_2O$); 3.91 (4H, t, *J* = 4.5, $2SCH_2C\underline{H}_2O$); 5.13 (4H, s, SCH_2NCH_2S); 6.82–7.31 (5H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 29.4 ($2S\underline{C}H_2CH_2O$); 55.2 (SCH_2NCH_2S); 70.3 ($O(\underline{C}H_2)_2O$); 74.8 ($2SCH_2\underline{C}H_2O$); 113.4 (C Ph); 118.3 (C Ph); 129.2 (C Ph); 145.7 (C Ph). Mass spectrum, *m/z* (I_{rel}, %): 300 (100) $[M+H]^+$. Found, *m/z*: 300.095 $[M+H]^+$. $C_{14}H_{22}NO_2S_2$. Calculated, *m/z*: 300.109. Found, %: C 56.27; H 6.98; N 4.74; S 21.56. $C_{14}H_{21}NO_2S_2$. Calculated, %: C 56.15; H 7.07; N 4.68; S 21.41.

Cyclothiomethylation of nitroanilines 4a–g with CH_2O and 1,2-ethanedithiol (General method). A mixture of 1,2-ethanedithiol (0.08 ml, 1 mmol) and 37% formalin (0.15 ml, 2 mmol) was stirred for 30 min at room temperature. A solution of nitroaniline **4a**–**g** (1 mmol) in the appropriate solvent (5 ml) (compounds **4a**–**e** – EtOAc, compound **4f** – $CHCl_3$, compound **4g** – Me_2CO) was added dropwise and the mixture was stirred for 3–4 h at room temperature. The product was evaporated on a rotary evaporator and purified by column chromatography.

3-(2-Nitrophenyl)-1,5,3-dithiazepane (5a). Yield 0.22 g (86%), yellow powder, mp 80–82°C (PhH–Me_2CO, 2:1) (mp 81–83°C[21a]), R_f 0.90 (PhH–Me_2CO, 2:1). IR spectrum, ν, cm^{-1}: 579 (C–S), 746 (C–S–C), 881 (C–N), 1124 (C–N), 1151 (C–N), 1456 (CH_2), 2854 (CH_2), 2926 (CH_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.89 (4H, s, $S(CH_2)_2S$); 4.58 (2H, s, $NC\underline{H}_{ax}H_{eq}S$) and 4.60 (2H, s, $NCH_{ax}\underline{H}_{eq}S$); 6.80 (1H, t, *J* = 7.5, H Ar); 7.03 (1H, d, *J* = 8.5, H Ar); 7.53 (1H, t, *J* = 7.5, H Ar); 8.22 (1H, d, *J* = 8.5, H Ar). ^{13}C NMR spectrum, δ, ppm: 31.2 ($S(CH_2)_2S$); 45.8 (SCH_2NCH_2S); 114.8 (C Ar); 117.0 (C Ar); 127.0 (C Ar); 133.3 (C Ar); 136.1 (C Ar); 143.2 (C Ar). Found, *m/z*: 255.074 $[M–H]^+$. $C_{10}H_{11}N_2O_2S_2$. Calculated, *m/z*: 255.026. Mass spectrum, *m/z*: 280.554 $[M+Na+H]^+$, 255.074 $[M–H]^+$. Found, %: C 46.77; H 4.80; N 11.02; S 25.32. $C_{10}H_{12}N_2O_2S_2$. Calculated, %: C 46.85; H 4.72; N 10.93; S 25.02.

3-(3-Nitrophenyl)-1,5,3-dithiazepane (5b).[21a] Yield 0.20 g (78%), yellow powder, mp 110–112°C (PhH–

Me_2CO, 1:1), R_f 0.93 (PhH–Me_2CO, 1:1). IR spectrum, ν, cm^{-1}: 579 (C–S), 623 (C–S), 667 (C–H), 735 (C–S–C), 881 (C–N), 1105 (C–N), 1135 (C–N), 1222 (C–N), 1244 (C–N), 1275 (C–N), 1346 (NO_2^-), 1428 (CH_2), 1456 (CH_2), 1522 (NO_2^-), 2855 (CH_2), 2924 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.08 (4H, s, $S(CH_2)_2S$); 4.91 (4H, s, SCH_2NCH_2S); 7.40 (1H, d, *J* = 8.0, H Ar); 7.52 (1H, t, *J* = 8.2, H Ar); 7.65 (1H, d, *J* = 8.8, H Ar); 7.70 (1H, s, H Ar). ^{13}C NMR spectrum, δ, ppm: 34.1 ($S(\underline{C}H_2)_2S$); 53.7 (SCH_2NCH_2S); 109.9 (C Ar); 113.4 (C Ar); 122.4 (C Ar); 130.4 (C Ar); 146.3 (C Ar); 149.1 (C Ar). Found, *m/z*: 255.009 $[M–H]^+$. $C_{10}H_{11}N_2O_2S_2$. Calculated, *m/z*: 255.026. Found, %: C 46.91; H 4.67; N 10.98; S 24.92. $C_{10}H_{12}N_2O_2S_2$. Calculated, %: C 46.85; H 4.72; N 10.93; S 25.02.

3-(4-Nitrophenyl)-1,5,3-dithiazepane (5c).[21a] Yield 0.22 g (85%), yellow powder, mp 148–150°C, R_f 0.93 (PhH–Me_2CO, 2:1). IR spectrum, ν, cm^{-1}: 610 (C–S), 754 (C–S–C), 830 (C–H), 1113 (C–N), 1146 (C–N), 1218 (C–N), 1273 (C–N), 1322 (C–N), 1459 (CH_2), 2854 (CH_2), 2924 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.09 (4H, s, $S(CH_2)_2S$); 4.84 (4H, s, SCH_2NCH_2S); 6.90 (2H, d, *J* = 9.2, H Ar); 8.20 (2H, d, *J* = 9.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 35.4 ($S(CH_2)_2S$); 53.6 (SCH_2NCH_2S); 113.8 (C Ar); 125.7 (C Ar); 139.6 (C Ar); 150.4 (C Ar). Mass spectrum, *m/z* (I_{rel}, %): 256 $[M]^+$ (85), 223 $[M–SH]^+$ (48), 106 $[C_6H_4NHCH_3]^+$ (93), 78 $[C_6H_6]^+$ (100). Found, %: C 46.76; H 4.79; N 10.85; S 25.14. $C_{10}H_{12}N_2O_2S_2$. Calculated, %: C 46.85; H 4.72; N 10.93; S 25.02.

3-(4-Methyl-3-nitrophenyl)-1,5,3-dithiazepane (5d). Yield 0.23 g (85%), yellow crystals, mp 146–148°C, R_f 0.93 (PhH–EtOAc–Me_2CO, 1:2:1). IR spectrum, ν, cm^{-1}: 632 (C–S), 731 (C–S–C), 1138 (C–N), 1214 (C–N), 1341 (NO_2^-), 1524 (NO_2^-), 2856 (CH_3). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, CH_3); 3.07 (4H, s, $S(CH_2)_2S$); 4.77 (4H, s, SCH_2NCH_2S); 7.03–7.06 (1H, m, H Ar); 7.24–7.51 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 19.6 (CH_3); 35.5 ($S(CH_2)_2S$); 54.5 (SCH_2NCH_2S); 111.3 (C Ar); 120.2 (C Ar); 124.1 (C Ar); 133.4 (C Ar); 144.4 (C Ar); 149.6 (C Ar). Mass spectrum, *m/z* (I_{rel}, %): 270 $[M]^+$ (100), 237 $[M–SH]^+$ (59), 106 $[C_6H_4NHCH_3]^+$ (73), 78 $[C_6H_6]^+$ (75). Found, %: C 48.81; H 5.17; N 10.28; S 23.79. $C_{11}H_{14}N_2O_2S_2$. Calculated, %: C 48.87; H 5.22; N 10.36; S 23.72.

3-(2-Methyl-3-nitrophenyl)-1,5,3-dithiazepane (5e). Yield 0.20 g (74%), yellow oil, R_f 0.85 (PhMe–EtOAc–Me_2CO, 1:2:1). IR spectrum, ν, cm^{-1}: 638 (C–S), 734 (C–S–C), 809 (C–H), 1125 (C–N), 1202 (C–N), 1281 (C–N), 1350 (NO_2^-), 1468 (CH_3), 1525 (NO_2^-), 2867 (CH_3). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.45 (3H, s, CH_3); 3.12 (4H, s, $S(CH_2)_2S$); 4.62 (4H, s, SCH_2NCH_2S); 7.32 (1H, t, *J* = 6.4, H Ar); 7.63 (1H, d, *J* = 6.4, H Ar); 7.69 (1H, d, *J* = 6.4, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.5 (CH_3); 37.6 ($S(CH_2)_2S$); 58.9 (SCH_2NCH_2S); 120.3 (C Ar); 126.7 (C Ar); 127.5 (C Ar); 128.8 (C Ar); 150.7 (C Ar); 151.6 (C Ar). Found, *m/z*: 269.041 $[M–H]^+$. $C_{11}H_{13}N_2O_2S_2$. Calculated, *m/z*: 269.042. Found, %: C 48.93; H 5.14; N 10.28; S 23.63. $C_{11}H_{14}N_2O_2S_2$. Calculated, %: C 48.87; H 5.22; N 10.36; S 23.72.

3-(4-Fluoro-3-nitrophenyl)-1,5,3-dithiazepane (5f). Yield 0.25 g (93%), yellow powder, mp 158–160°C, R_f 0.79 ($CHCl_3$–EtOAc, 1:1). IR spectrum, ν, cm^{-1}: 590 (C–S), 623 (C–S), 641 (C–S), 735 (C–S–C), 816 (C–H), 1142 (C–N), 1219 (C–N), 1240 (C–N), 1276 (C–F), 1346 (NO_2^-), 1416 (C–H), 1455 (CH_2), 1540 (NO_2^-). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.09 (4H, s, $S(CH_2)_2S$); 4.77 (4H, s, SCH_2NCH_2S); 7.13–7.55 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 35.5 (s, $S(CH_2)_2S$); 54.8 (s, SCH_2NCH_2S); 112.0 (d, $^4J_{CF}$ = 2.0, C Ar); 118.9 (d, $^2J_{CF}$ = 102.0, C Ar); 122.3 (d, $^3J_{CF}$ = 7.0, C Ar); 137.4 (s, C Ar); 142.2 (s, C Ar); 149.3 (d, $^1J_{CF}$ = 256.0, C–F). ^{19}F NMR spectrum, δ, ppm: –130.0. Found, *m/z*: 273.008 $[M–H]^+$. $C_{10}H_{10}FN_2O_2S_2$. Calculated, *m/z*: 273.017. Found, %: C 43.69; H 4.09; N 10.17; S 23.54. $C_{10}H_{11}FN_2O_2S_2$. Calculated, %: C 43.78; H 4.04; N 10.21; S 23.38.

4-(1,5,3-Dithiazepan-3-yl)-2-nitrophenol (5g). Yield 0.23 g (86%), red crystals, mp 186–188°C, R_f 0.90 ($CHCl_3$–EtOH, 2:1). UV spectrum, λ_{max}, nm: 258, 453. IR spectrum, ν, cm^{-1}: 567 (C–H), 618 (C–S), 681 (C–S), 755 (C–S–C), 817 (C–H), 861 (C–H), 1079 (C–OH), 1200 (C–N), 1227 (C–N), 1251 (C–N), 1304 (CH_2), 1423 (CH_2), 1531 (NO_2^-), 2854 (CH_2), 2924 (CH_2), 3083 (=C–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.07 (4H, s, $S(CH_2)_2S$); 4.79 (4H, s, SCH_2NCH_2S); 7.06 (1H, d, *J* = 7.6, H Ar); 7.27 (1H, dd, ^1J = 7.4, ^2J = 2.4, H Ar); 7.38 (1H, d, *J* = 2.4, H Ar); 8.31 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 34.3 ($S(CH_2)_2S$); 54.5 (SCH_2NCH_2S); 111.3 (C Ar); 120.1 (C Ar); 124.8 (C Ar); 136.9 (C Ar); 138.4 (C Ar); 145.8 (C Ar). Found, *m/z*: 271.013 $[M–H]^+$. $C_{10}H_{11}N_2O_3S_2$. Calculated, *m/z*: 271.021. Found, %: C 44.18; H 4.39; N 10.32; S 23.43. $C_{10}H_{12}N_2O_3S_2$. Calculated, %: C 44.10; H 4.44; N 10.29; S 23.55.

Cyclothiomethylation of nitroanilines 4f,g with CH_2O and aliphatic α,ω-dithiols (General method). A mixture of the appropriate α,ω-dithiol (1 mmol) and 37% formalin (0.15 ml, 2 mmol) was stirred for 30 min at room temperature. Then a solution of nitroaniline **4f**,**g** (1 mmol) and $SmCl_3·6H_2O$ (0.02 g, 5 mol %) in 5 ml of suitable solvent (compound **4f** – $CHCl_3$, compound **4g** – Me_2CO) was added dropwise. The mixture was stirred for 3–4 h at 40°C, then evaporated on a rotary evaporator. The product was purified by column chromatography.

3-(4-Fluoro-3-nitrophenyl)-1,5,3-dithiazocane (6a). Yield 0.26 g (90%), yellow powder, mp 125–127°C, R_f 0.80 (PhH–EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 624 (C–S), 705 (C–S), 733 (C–S–C), 812 (C–H), 847 (C–N), 970 (C–H), 1148 (C–N), 1241 (C–N), 1282 (C–F), 1350 (NO_2^-), 1540 (NO_2^-). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.83–1.89 (2H, m, $SCH_2C\underline{H}_2CH_2S$); 2.71 (4H, t, *J* = 5.8, $SC\underline{H}_2CH_2C\underline{H}_2S$); 4.77 (4H, s, SCH_2NCH_2S); 7.13–7.52 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.1 (s, $SCH_2\underline{C}H_2CH_2S$); 31.9 (s, $S\underline{C}H_2CH_2\underline{C}H_2S$); 56.7 (s, SCH_2NCH_2S); 109.6 (d, $^4J_{CF}$ = 3.0, C Ar); 119.0 (d, $^2J_{CF}$ = 21.9, C Ar); 119.9 (d, $^3J_{CF}$ = 7.2, C Ar); 137.9 (s, C Ar); 139.9 (s, C Ar); 148.9 (d, $^1J_{CF}$ = 255.7, C–F). Found, *m/z*: 289.220 $[M+H]^+$. $C_{11}H_{14}FN_2O_2S_2$. Calculated, *m/z*: 289.048. Found, %: C 45.78; H 4.60; N 9.67; S 22.11. $C_{11}H_{13}FN_2O_2S_2$. Calculated, %: C 45.82; H 4.54; N 9.71; S 22.24.

3-(4-Fluoro-3-nitrophenyl)-1,5,3-dithiazonane (6b). Yield 0.22 g (73%), yellow oil, R_f 0.82 (PhH–EtOAc, 3:1).

IR spectrum, ν, cm^{-1}: 596 (C–S), 755 (C–S–C), 815 (C–H), 1140 (C–N), 1219 (C–N), 1243 (C–N), 1273 (C–F), 1348 (NO_2^-), 1418 (C–H), 1454 (CH_2), 1538 (NO_2^-), 1672 (C=C), 2854 (CH_2), 3065 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.71 (4H, br. s, $SCH_2C\underline{H}_2C\underline{H}_2CH_2S$); 2.56 (4H, br. s, $SC\underline{H}_2(CH_2)_2C\underline{H}_2S$); 4.61–4.63 (4H, m, SCH_2NCH_2S); 7.18–7.22 (2H, m, H Ar); 7.56 (1H, br. s, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 28.8 (s, $SCH_2\underline{C}H_2\underline{C}H_2CH_2S$); 31.1 (s, $S\underline{C}H_2(CH_2)_2\underline{C}H_2S$); 54.4 (s, SCH_2NCH_2S); 111.7 (br. s, C Ar); 118.9 (d, $^2J_{CF}$ = 22.0, C Ar); 122.0 (d, $^3J_{CF}$ = 7.2, C Ar); 137.4 (s, C Ar); 143.0 (s, C Ar); 149.1 (d, $^1J_{CF}$ = 257.0, C–F). Found, *m*/*z*: 302.202 $[M]^+$. $C_{12}H_{15}FN_2O_2S_2$. Calculated, *m*/*z*: 302.056. Found, %: C 47.71; H 5.07; N 9.19; S 21.33. $C_{12}H_{15}FN_2O_2S_2$. Calculated, %: C 47.66; H 5.00; N 9.26; S 21.21.

3-(4-Fluoro-3-nitrophenyl)-1,5,3-dithiazecane (6c). Yield 0.23 g (76%), yellow oil, R_f 0.83 (PhH–CH_2Cl_2–EtOAc, 3:1:1). IR spectrum, ν, cm^{-1}: 597 (C–S), 734 (C–S–C), 815 (C–H), 1139 (C–N), 1217 (C–N), 1243 (C–N), 1348 (CH_2), 1419 (C–H), 1456 (CH_2), 1537 (NO_2^-), 2854 (CH_2), 2925 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.49–1.51 (2H, m, $S(CH_2)_2C\underline{H}_2(CH_2)_2S$); 1.62 (4H, br. s, $SCH_2C\underline{H}_2CH_2C\underline{H}_2CH_2S$); 2.51–2.60 (4H, m, $SC\underline{H}_2(CH_2)_3C\underline{H}_2S$); 4.62 (4H, s, SCH_2NCH_2S); 7.17–7.22 (2H, m, H Ar); 7.57 (1H, br. s, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 28.0 (s, $S(CH_2)_2\underline{C}H_2(CH_2)_2S$); 29.4 (s, $SCH_2\underline{C}H_2CH_2\underline{C}H_2CH_2S$); 31.4 (s, $S\underline{C}H_2(CH_2)_3\underline{C}H_2S$); 54.4 (s, SCH_2NCH_2S); 111.6 (br. s, C Ar); 118.9 (d, $^2J_{CF}$ = 21.9, C Ar); 121.9 (d, $^3J_{CF}$ = 7.0, C Ar); 137.3 (s, C Ar); 143.0 (s, C Ar); 149.1 (d, $^1J_{CF}$ = 256.5, C–F). Found, *m*/*z*: 317.333 $[M+H]^+$. $C_{13}H_{18}N_2O_2S_2$. Calculated, *m*/*z*: 317.079. Found, %: C 49.43; H 5.37; N 8.94; S 20.39. $C_{13}H_{17}N_2O_2S_2$. Calculated, %: C 49.35; H 5.42; N 8.85; S 20.27.

3-(4-Fluoro-3-nitrophenyl)-1,5-dithia-3-azacycloundecane (6d). Yield 0.24 g (71%), yellow oil, R_f 0.88 (PhH–CH_2Cl_2–EtOAc, 4:1:1). IR spectrum, ν, cm^{-1}: 670 (C–S), 736 (C–S–C), 815 (C–H), 1150 (C–N), 1220 (C–N), 1244 (C–N), 1272 (C–F), 1347 (NO_2^-), 1420 (C–H), 1458 (CH_2), 1537 (NO_2^-), 2854 (CH_2), 2924 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.33–1.40 (4H, m, $S(CH_2)_2C\underline{H}_2C\underline{H}_2(CH_2)_2S$); 1.62 (4H, br. s, $SCH_2C\underline{H}_2(CH_2)_2C\underline{H}_2CH_2S$); 2.51–2.61 (4H, m, $SC\underline{H}_2(CH_2)_4C\underline{H}_2S$); 4.62 (4H, s, SCH_2NCH_2S); 7.18–7.23 (2H, m, H Ar); 7.57 (1H, br. s, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 28.4 (s, $S(CH_2)_2\underline{C}H_2\underline{C}H_2(CH_2)_2S$); 29.7 (s, $SCH_2\underline{C}H_2(CH_2)_2\underline{C}H_2CH_2S$); 31.5 (s, $S\underline{C}H_2(CH_2)_4\underline{C}H_2S$); 54.3 (s, SCH_2NCH_2S); 111.6 (br. s, C Ar); 118.9 (d, $^2J_{CF}$ = 21.9, C Ar); 121.9 (d, $^3J_{CF}$ = 5.7, C Ar); 137.3 (s, C Ar); 143.1 (s, C Ar); 149.1 (d, $^1J_{CF}$ = 255.9, C–F). Found, *m*/*z*: 331.225 $[M+H]^+$. $C_{14}H_{20}FN_2O_2S_2$. Calculated, *m*/*z*: 331.095. Found, %: C 50.96; H 5.74; N 8.55; S 19.30. $C_{14}H_{19}FN_2O_2S_2$. Calculated, %: C 50.89; H 5.80; N 8.48; S 19.41.

3-(4-Fluoro-3-nitrophenyl)-1,5-dithia-3-azacyclotridecane (6e). Yield 0.20 g (56%), yellow oil, R_f 0.88 (PhH–CH_2Cl_2–EtOAc, 5:1:1). IR spectrum, ν, cm^{-1}: 756 (C–S), 814 (C–H), 1077 (C–N), 1243 (C–N), 1271 (C–F), 1347 (NO_2^-), 1420 (C–H), 1460 (CH_2), 1536 (NO_2^-), 2853 (CH_2), 2925 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.25–1.30 (4H, m, $S(CH_2)_3C\underline{H}_2C\underline{H}_2(CH_2)_3S$); 1.34–1.37 (4H, m, $S(CH_2)_2C\underline{H}_2(CH_2)_2C\underline{H}_2(CH_2)_2S$); 1.59–1.62 (4H, m, $SCH_2C\underline{H}_2(CH_2)_4C\underline{H}_2CH_2S$); 2.56–2.60 (4H, m, $SC\underline{H}_2(CH_2)_6C\underline{H}_2S$); 4.63 (4H, s, SCH_2NCH_2S); 7.18–7.22 (2H, m, H Ar); 7.58–7.59 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 28.8 (s, $S(CH_2)_3\underline{C}H_2\underline{C}H_2(CH_2)_3S$); 29.0 (s, $S(CH_2)_2\underline{C}H_2(CH_2)_2\underline{C}H_2(CH_2)_2S$); 29.8 (s, $SCH_2\underline{C}H_2(CH_2)_4\underline{C}H_2CH_2S$); 31.6 (s, $S\underline{C}H_2(CH_2)_6\underline{C}H_2S$); 54.3 (s, SCH_2NCH_2S); 111.6 (br. s, C Ar); 118.8 (d, $^2J_{CF}$ = 17.5, C Ar); 121.8 (d, $^3J_{CF}$ = 2.2, C Ar); 137.4 (s, C Ar); 143.2 (s, C Ar); 149.1 (d, $^1J_{CF}$ = 205.7, C–F). Found, *m*/*z*: 358.155 $[M]^+$. $C_{16}H_{23}FN_2O_2S_2$. Calculated, *m*/*z*: 358.118. Found, %: C 53.67; H 6.54; N 7.75; S 17.76. $C_{16}H_{23}FN_2O_2S_2$. Calculated, %: C 53.61; H 6.47; N 7.81; S 17.89.

4-(1,5,3-Dithiazocan-3-yl)-2-nitrophenol (7a). Yield 0.26 g (91%), red crystals, mp 167–169°C, R_f 0.69 (PhH–Me_2CO, 4:1). IR spectrum, ν, cm^{-1}: 561 (C–H), 587 (C–S), 669 (C–H), 757 (C–S–C), 821 (C–H), 1077 (C–OH), 1143 (C–N), 1215 (C–N), 1308 (CH_2), 1426 (CH_2), 1537 (NO_2^-), 2853 (CH_2), 2925 (CH_2), 3019 (=C–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.85 (2H, q, *J* = 5.8, $SCH_2C\underline{H}_2CH_2S$); 2.72 (4H, t, *J* = 5.8, $SC\underline{H}_2CH_2C\underline{H}_2S$); 4.77 (4H, s, SCH_2NCH_2S); 7.16–7.54 (3H, m, H Ar); 10.22 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.1 ($SCH_2\underline{C}H_2CH_2S$); 32.1 ($S\underline{C}H_2CH_2\underline{C}H_2S$); 56.7 ($SCH_2NCH_2S$); 107.3 (C Ar); 120.6 (C Ar); 124.3 (C Ar); 133.8 (C Ar); 136.8 (C Ar); 148.5 (C Ar). Found, *m*/*z*: 287.095 $[M+H]^+$. $C_{11}H_{15}N_2O_3S_2$. Calculated, *m*/*z*: 287.052. Found, %: C 46.21; H 4.87; N 9.84; S 22.23. $C_{11}H_{14}N_2O_3S_2$. Calculated, %: C 46.14; H 4.93: N 9.78; S 22.39.

4-(1,5,3-Dithiazonan-3-yl)-2-nitrophenol (7b). Yield 0.20 g (67%), red oil, R_f 0.83 (PhH–Me_2CO, 5:1). IR spectrum, ν, cm^{-1}: 561 (C–H), 587 (C–S), 669 (C–H), 756 (C–S–C), 822 (C–H), 887 (C–H), 1077 (C–OH), 1142 (C–N), 1215 (C–N), 1308 (CH_2), 1426 (CH_2), 1537 (NO_2^-), 2854 (CH_2), 3019 (=C–H). ^{1}H NMR spectrum, δ, ppm: 1.69 (4H, br. s, $SCH_2C\underline{H}_2C\underline{H}_2CH_2S$); 2.56 (4H, br. s, $SC\underline{H}_2(CH_2)_2C\underline{H}_2S$); 4.57–4.60 (4H, m, SCH_2NCH_2S); 7.08–7.10 (1H, m, H Ar); 7.28–7.30 (1H, m, H Ar); 7.58 (1H, s, H Ar); 10.21 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 28.8 ($SCH_2\underline{C}H_2\underline{C}H_2CH_2S$); 31.1 ($S\underline{C}H_2(CH_2)_2\underline{C}H_2S$); 54.5 ($SCH_2NCH_2S$); 110.5 (C Ar); 120.6 (C Ar); 127.4 (C Ar); 133.5 (C Ar); 140.2 (C Ar); 149.2 (C Ar). Found, *m*/*z*: 299.153 $[M–H]^+$. $C_{12}H_{15}N_2O_3S_2$. Calculated, *m*/*z*: 299.052. Found, %: C 47.89; H 5.44; N 9.40; S 21.23. $C_{12}H_{16}N_2O_3S_2$. Calculated, %: C 47.98; H 5.37; N 9.33; S 21.35.

4-(1,5,3-Dithiazecan-3-yl)-2-nitrophenol (7c). Yield 0.18 g (57%), red oil, R_f 0.88 (PhH–Me_2CO, 6:1). IR spectrum, ν, cm^{-1}: 561 (C–H), 588 (C–S), 669 (C–H), 757 (C–S–C), 822 (C–H), 1077 (C–OH), 1141 (C–N), 1215 (C–N), 1307 (CH_2), 1427 (CH_2), 1537 (NO_2), 2856 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.46–1.48 (2H, m, $S(CH_2)_2C\underline{H}_2(CH_2)_2S$); 1.58–1.61 (4H, m, $SCH_2C\underline{H}_2CH_2C\underline{H}_2CH_2S$); 2.49–2.57 (4H, m, $SC\underline{H}_2(CH_2)_3C\underline{H}_2S$); 4.58 (4H, s, SCH_2NCH_2S); 7.08–7.10 (1H, m, H Ar); 7.28–7.31 (1H, m, H Ar); 7.58 (1H, s, H Ar); 10.21–10.23 (1H, m, OH). ^{13}C NMR spectrum, δ, ppm: 28.0 ($S(CH_2)_2\underline{C}H_2(CH_2)_2S$); 29.4 ($SCH_2\underline{C}H_2CH_2\underline{C}H_2CH_2S$); 31.4 ($S\underline{C}H_2(CH_2)_3\underline{C}H_2S$); 54.4 ($SCH_2NCH_2S$); 110.3 (C Ar); 120.5 (C Ar); 127.3 (C Ar); 133.4 (C Ar); 140.3 (C Ar); 149.2 (C Ar). Found, *m*/*z*: 313.143 $[M–H]^+$. $C_{13}H_{17}N_2O_3S_2$.

Calculated, *m/z*: 313.068. Found, %: C 49.58; H 5.84; N 8.85; S 20.52. $C_{13}H_{18}N_2O_3S_2$. Calculated, %: C 49.66; H 5.77; N 8.91; S 20.40.

4-(1,5-Dithia-3-azacycloundecanyl)-2-nitrophenol (7d). Yield 0.22 g (67%), red oil, R_f 0.88 (PhH–CH_2Cl_2–Me_2CO, 4:1:1). IR spectrum, ν, cm^{-1}: 561 (C–H), 587 (C–S), 663 (C–S), 672 (C–H), 757 (C–S–C), 822 (C–H), 1076 (C–OH), 1142 (C–N), 1205 (C–OH), 1237 (C–N), 1304 (CH_2), 1425 (CH_2), 1536 (NO_2^-), 2854 (CH_2), 2924 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.34–1.35 (4H, m, $S(CH_2)_2C\underline{H}_2C\underline{H}_2(CH_2)_2S$); 1.54–1.57 (4H, m, $SCH_2C\underline{H}_2(CH_2)_2C\underline{H}_2CH_2S$); 2.47–2.53 (4H, m, $SC\underline{H}_2(CH_2)_4C\underline{H}_2S$); 4.57 (4H, s, SCH_2NCH_2S); 7.07 (1H, d, *J* = 8.8, H Ar); 7.27 (1H, d, *J* = 8.8, H Ar); 7.56 (1H, s, H Ar); 10.19 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 28.4 ($S(CH_2)_2\underline{C}H_2\underline{C}H_2(CH_2)_2S$); 29.7 ($SCH_2\underline{C}H_2(CH_2)_2\underline{C}H_2CH_2S$); 31.5 ($S\underline{C}H_2(CH_2)_4\underline{C}H_2S$); 54.4 ($SCH_2NCH_2S$); 110.3 (C Ar); 120.5 (C Ar); 127.3 (C Ar); 133.4 (C Ar); 140.3 (C Ar); 149.0 (C Ar). Found, *m/z*: 329.215 $[M+H]^+$. $C_{14}H_{21}N_2O_3S_2$. Calculated, *m/z*: 329.099. Found, %: C 51.27; H 6.09; N 8.61; S 19.43. $C_{14}H_{20}N_2O_3S_2$. Calculated, %: C 51.20; H 6.14; N 8.53; S 19.52.

Cyclothiomethylation of nitroanilines 4f,g with CH_2O and 3,6-dioxa-1,8-octanedithiol (General method). A mixture of 3,6-dioxa-1,8-octanedithiol (0.16 ml, 1 mmol) and 37% formalin (0.15 ml, 2 mmol) was stirred for 30 min at room temperature. Then a solution of nitroaniline **4f**,**g** (1 mmol) and $SmCl_3 \cdot 6H_2O$ (0.02 g, 5 mol %) in 5 ml of suitable solvent (compound **4f** – $CHCl_3$, compound **4g** – Me_2CO) was added dropwise. The mixture was stirred for 3–4 h at 40°C, the product was then evaporated on a rotary evaporator and purified by column chromatography.

3-(4-Fluoro-3-nitrophenyl)-1,11-dioxa-4,8-dithia-6-aza-cyclotridecane (8a). Yield 0.27 g (74%), yellow powder, mp 114–117°C, R_f 0.76 (PhH–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 549 (C–H), 592 (C–S), 686 (C–S), 707 (C–H), 756 (C–S–C), 807 (C–H), 1072 (C–O–C), 1112 (C–N), 1138 (C–O–C), 1215 (C–N), 1245 (NO_2^-), 1266 (C–O–C), 1281 (C–F), 1349 (NO_2^-), 1386 (O–H), 1422 (C–OH), 1450 (CH_2), 1539 (NO_2^-). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.69 (4H, t, *J* = 4.6, $2SC\underline{H}_2CH_2O$); 3.71 (4H, s, OCH_2CH_2O); 3.92 (4H, t, *J* = 4.6, $2SCH_2C\underline{H}_2O$); 5.11 (4H, s, SCH_2NCH_2S); 7.15–7.22 (2H, m, H Ar); 7.60–7.62 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 29.2 ($2S\underline{C}H_2CH_2O$); 55.0 (SCH_2NCH_2S); 70.2 (OCH_2CH_2O); 74.8 ($2SCH_2\underline{C}H_2O$); 109.5 (d, $^4J_{CF}$ = 2.2, C Ar); 118.7 (d, $^2J_{CF}$ = 17.4, C Ar); 119.8 (d, $^3J_{CF}$ = 5.5, C Ar); 137.5 (d, J_{CF} = 6.1, C Ar); 142.5 (s, C Ar); 148.5 (d, $^1J_{CF}$ = 203.6, C Ar). ^{19}F NMR spectrum, δ, ppm: –132.9. Found, *m/z*: 361.039 $[M–H]^+$. $C_{14}H_{18}FN_2O_4S_2$. Calculated, *m/z*: 361.069. Found, %: C 46.45; H 5.22; N 7.81; S 17.76. $C_{14}H_{19}FN_2O_4S_2$. Calculated, %: C 46.39; H 5.28; N 7.73; S 17.69.

4-(1,11-Dioxa-4,8-dithia-6-azacyclotridecanyl)-2-nitro-phenol (8b). Yield 0.28 g (78%), red powder, mp 126–129°C, R_f 0.90 (PhH–CH_2Cl_2–Me_2CO, 4:1:1). IR spectrum, ν, cm^{-1}: 561 (C–H), 585 (C–S), 649 (C–S), 756 (C–S–C), 821 (C–H), 847 (C–N), 1075 (C–OH), 1114 (C–N), 1140 (C–O–C), 1206 (C–N), 1237 (C–N), 1280 (C–O–C), 1349 (NO_2^-), 1426 (CH_2), 1536 (NO_2^-), 2855 (CH_2), 2924 (CH_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.66 (4H, t, *J* = 4.6, $2SC\underline{H}_2CH_2O$); 3.68 (4H, s, OCH_2CH_2O); 3.89 (4H, t, *J* = 4.6, $2SCH_2C\underline{H}_2O$); 5.07 (4H, s, SCH_2NCH_2S); 7.07 (1H, d, *J* = 9.2, H Ar); 7.33–7.34 (1H, m, H Ar); 7.59 (1H, d, *J* = 2.8, H Ar); 10.15 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 29.2 ($2S\underline{C}H_2CH_2O$); 55.1 (SCH_2NCH_2S); 70.2 (OCH_2CH_2O); 74.8 ($2SCH_2\underline{C}H_2O$); 107.0 (C Ar); 120.3 (C Ar); 124.6 (C Ar); 133.7 (C Ar); 139.5 (C Ar); 148.1 (C Ar). Found, *m/z*: 359.120 $[M–H]^+$. $C_{14}H_{19}N_2O_5S_2$. Calculated, *m/z*: 359.074. Found, %: C 46.72; H 5.63; N 7.69; S 17.65. $C_{14}H_{20}N_2O_5S_2$. Calculated, %: C 46.65; H 5.59; N 7.77; S 17.79.

A study of the sorption properties of compounds 2a and 3. The sorption properties of compounds **2a**, **3** were studied by static method of separately weighed samples at 20 ± 0.5°C temperature at the stirring rate of 800 rpm (MM 2A magnetic stirrer) and phase contact duration of 20 min for palladium(II), 60 min for silver(I).

X-ray structural study of compounds 2a,b, 3, 5d,g, 8b. Crystals of compounds suitable for X-ray structural analysis were obtained by slow evaporation of eluent at room temperature: compound **2a** – *n*-C_6H_{14}–$CHCl_3$, 1:2; compound **2b** – PhH–$CHCl_3$, 1:1; compound **3** – *cyclo*-C_6H_{12}–CH_2Cl_2, 1:1; compound **5d** – PhH–EtOAc–Me_2CO, 1:2:1; compound **5g** – $CHCl_3$–EtOH, 2:1; compound **8b** – PhH–CH_2Cl_2–Me_2CO, 4:1:1. The study was performed on an Xcalibur Gemini diffractometer, equipped with an Eos CCD detector (graphite monochromator, MoKα radiation, λ 0.71073 Å, ω-scanning, $2\theta_{max}$ 62°). The data collection and processing were performed by using the CrysAlis^{Pro} software from Oxford Diffraction Ltd.[28] The structures were solved by direct method and refined by full-matrix method of least squares in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were localized by differential Fourier synthesis and refined isotropically. The calculations were performed with SHELX software.[29] The complete X-ray diffraction dataset was deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1471862 (compound **2a**), CCDC 1471855 (compound **2b**), CCDC 1471853 (compound **3**), CCDC 1474965 (compound **5d**), CCDC 1471945 (compound **5g**), and CCDC 1471852 (compound **8b**)).

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