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N,N,N′,N′-Tetramethylmethanediamine, Efficient Reagent for Thioles Aminomethylation

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Abstract—Efficient method was developed for thiols aminomethylation using *N,N,N′,N′*-tetra-methylmethanediamine in the presence of Sm and Fe salts. Aminosulfides were obtained in high yields and selectivity.

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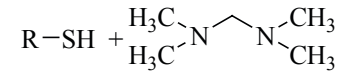
Organic compounds containing nitrogen and sulfur are used as efficient plant protecting substances[1–3], antioxidants, anticorrosion, antiscoring, and antiwear additives to fuels and lubricants [4–10].

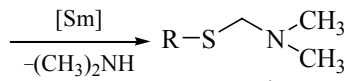
Up to now one of the most known methods for the synthesis of aminosulfides remains the classic Mannich aminomethylation of thiols by secondary amines and aldehydes [11], but this procedure possesses certain limitations. For instance, the thiols aminomethylation using formaldehyde and dimethylamine occurs with relatively low yields [12] due to the application and dosing of the water solutions of the initial reagents. We report here on a new approach to aminomethylation of mono- and dithiols applying an available and industrially produced *N,N,N′,N′*-tetramethylmethanediamine that exhibits a high reactivity in the catalyzed aminomethylation of terminal acetylenes with the use of *gem*-diamines [13–15].

By an example of the reaction of pentylmercaptan with diamine it was established that among the tested catalysts based on halides and complexes of Cu, Sm, Fe, Co, Mn, Pd, V, Zr, Ti the highest activity exhibited $SmCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$. In the presence of $SmCl_3 \cdot 6H_2O$ (the ratio [pentylmercaptan] : [diamine] : [Sm] 10 : 12 : 0.5, 60°C, 1.5 h, solvent) in the argon atmosphere *N,N*-dimethyl-1-(pentylsulfanyl)methanamine (**Ia**) formed in 98% yield, and in the presence of $FeCl_3 \cdot 6H_2O$ in analogous conditions, in 95% yield. The use as solvents of benzene and DMF reduced the yield of aminosulfide **Ia** to 50%. The yield is fairly sensitive to the nature of the anion at the central atom of the catalyst: $SmCl_3 \cdot 6H_2O$ (98%), $Sm(NO_3)_3 \cdot 6H_2O$ (60%), $Sm(acac)_3 \cdot H_2O$ (43%).

Without catalyst under the mentioned conditions aminosulfide **Ia** formed in the yield not exceeding 40%. In this reaction $CoCl_2$, CuCl, $CuCl_2 \cdot 2H_2O$, $NiCl_2$, $MnCl_2 \cdot 2H_2O$, $PdCl_2$, $ZnCl_2$ did not show any considerable catalytic activity.

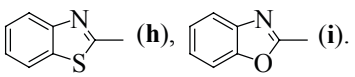
In the developed optimal conditions (5 mol% $SmCl_3 \cdot 6H_2O$, 60°C, 1.5 h, $CHCl_3$) the aminomethylation of butyl-, heptyl-, isopropyl-, *tert*-butyl-, phenyl-, benzyl-, 1,3-benzothiazol-2-yl-, 1,3-benzoxazol-2-ylthiols with the help of the diamine (molar ratio thiol–diamine 10 : 12) resulted in corresponding aminosulfides **Ib–Ii** in 84–98% yields.





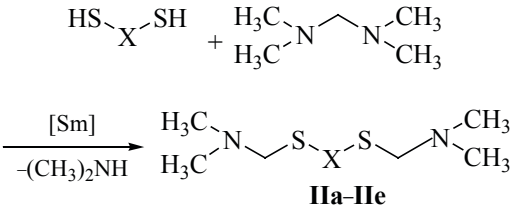
Ia–Ii

R = C_5H_{11} (**a**), C_4H_9 (**b**), C_7H_{15} (**c**), *i*-Pr (**d**), *t*-Bu (**e**), Ph (**f**), Bn (**g**),



The formation of compounds **Ia–Ii** is confirmed by the appearance in the ^{1}H and ^{13}C NMR spectra of signals at δ_H 3.67–3.93 and δ_C 59.94–69.01 ppm of the fragment SCH_2N. In the IR spectra the characteristic absorption bands of the stretching vibrations of the C–S bond in the region 646–647 cm^{-1} indicate the presence of the thioether group [16]. The mass spectra of compounds **Ia–Ic** contain the peaks of molecular ions, *m/z* 161 (**Ia**), 147 (**Ib**), 189 (**Ic**), and of fragment ions $[M - (CH_3)_2NCH_2 + H]^+$ 104 (**Ia**), 90 (**Ib**), 132 (**Ic**), $[M - H]^+$ 223.682 (**Ih**) and 207.646 (**Ii**).

Aiming at the development of a selective procedure of the synthesis of diaminodisulfides we explored the aminomethylation of dithiols with *N,N,N′,N′*-tetramethylmethanediamine. At the aminomethylation of dithiols (1,2-ethane-, 1,3-propane-, 1,4-butane-, 3,6-dioxa-1,8-octanedithiol, 4,4′-oxydithiophenol) with the diamine (the ratio [dithiol] : [diamine] : [Sm] = 10 : 22 : 0.5, 60°C, 1.5 h, solvent $CHCl_3$) diaminodisulfides **IIa–IIe** formed in 80– 94% yields.



IIa–IIe

X = $(CH_2)_n$, n = 2 (**a**), 3 (**b**), 4 (**c**), $(CH_2)_2O(CH_2)_2O(CH_2)_2$ (**d**), *p*-$C_6H_4OC_6H_4$-*p* (**e**).

In the ^{1}H and ^{13}C NMR spectra of compounds **IIa–IIe** the signals at δ_H 3.43 – 4.53 and δ_C 64.06–64.91 ppm correspond to the fragment SCH_2N. The molecule is symmetric, and all the signals are magnetically equivalent. In the 2D-spectra HMBC of compound **IIe** cross-peaks are observed corresponding to the coupling of the atoms C^5–H^9 and C^9–H^{11} (C^{11}–H^9) (see the figure).

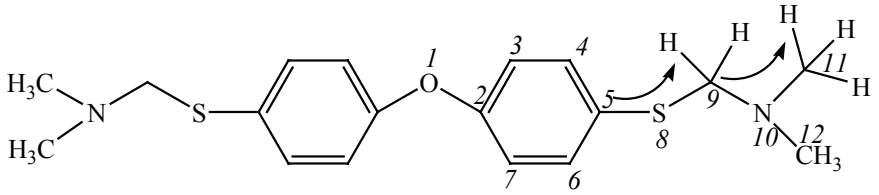
At the aminomethylation of 1,2-ethanedithiol with the diamine in the absence of solvent a mixture of polysulfides formed (mp 105–110°C) of low solubility in organic solvents.

For comparison of the rate of accumulation of compound **Ia** in the catalyzed and noncatalyzed reaction the aminomethylation of $C_5H_{11}SH$ with the diamine was carried out directly in the nmr tubes. It was found that after mixing the initial reagents signals appeared in the ^{1}H and ^{13}C NMR spectra at δ_H 3.9, δ_C 64.12 ppm and δ_H 2.4, δ_C 38.51 ppm belonging respectively to aminosulfide **Ia** and dimethylamine. The comparison of the intensity of the corresponding signals in the NMR spectra showed that the catalyst accelerated the formation of compound **Ia** more than twice.

Hence the thiols aminomethylation with the help of *N,N,N′,N′*-tetramethylmethanediamine using as catalysts $SmCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ is an efficient procedure of the synthesis of aminosulfides with high yields and selectivity.

EXPERIMENTAL

The reaction progress was monitored by TLC on Sorbfil plates, eluent hexane–ethyl acetate, 2 : 1. Initial compounds used in the study were of the purity ≥99%. The solvents were purified by standard procedures [16]. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 at operating frequencies 300.13 and 100.62 MHz, solvent $CDCl_3$ (δ_C 77.10 ppm). IR spectra were recorded on a spectrophotometer Bruker Vertex 70 v from mulls in mineral oil. Mass spectra of compounds **Ia–Ic** were measured on an instrument Shimadzu GCMS-QP2010Plus (capillary column SPB-5 30 m × 0.25 mm, carrier gas helium, ramp from 40 to 300°C at a rate 8 deg/min, vaporizer temperature 280°C, ion source temperature 200°C, ionizing energy 70 eV). Mass spectra of compounds **Ie, If** were obtained on a spectrometer MALDI-TOF Autoflex III (Bruker, Germany), α-cyano-4-hydroxycinnamic and 2,5-dihydrobenzoic acids were used as matrices (the sample was prepared by the method



2D (HMBC) couplings 4,4′-oxybis[phenyl-1-sulfanyl-(*N,N*-dimethyl)methaneamine] (**IIe**).

of "dried drop" in chloroform, 1 : 10). The elemental composition was determined on an analyzer Karlo Erba-1106, melting points, on an instrument RNMK 80/2617, refraction indices, on a refractometer IRF 454 BM. Individual substances were obtained by chromatography on silica gel of KSK grade (50 – 160 μm).

Aminomethylation of mercaptans with *N,N,N′,N′*-tetramethylmethanediamine. A mixture of 10 mmol of an appropriate mercaptan, 12 mmol of *N,N,N′,N′*-tetramethylmethanediamine, 0.5 mmol of catalyst $SmCl_3 \cdot 6H_2O$ or $FeCl_3 \cdot 6H_2O$ was stirred for 1.5 h at 60°C. Then from the reaction mixture *N,N*-dimethyl-*N*-[(alkylsulfanyl)methan]amines **I** were isolated by column chromatography on SiO_2.

***N,N*-Dimethyl-1-(pentylsulfanyl)methanamine (Ia).** Yield 98% ($SmCl_3 \cdot 6H_2O$), 95% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.4672, R_f 0.36. IR spectrum, cm^{-1}: 2929–2771, 1688, 1453, 1253, 1151, 1042, 816, 646. ^{1}H NMR spectrum, δ, ppm: 0.88 m (3H, CH_3), 1.32 m (4H, CH_2), 1.57 m (2H, CH_2), 2.20 br.s (6H, CH_3), 2.55 t (2H, CH_2), 3.93 br.s (2H, CH_2). ^{13}C NMR spectrum, δ, ppm: 13.65 s (C^{8}), 22.03 s (C^{7}), 30.07 s (C^{6}), 30.83 s (C^{5}), 33.27 s (C^{4}), 42.45 s (C$^{9,9'}$), 64.27 s (C^{2}). Mass spectrum, *m/z*: 161 $[M]^+$, 104 $[M - (CH_3)_2NCH_2 + H]^+$, 58 $[M - C_5H_{11}S]^+$. Found, %: C 58.32; H 11.24; N 10.27; S 20.17. $C_8H_{19}NS$. Calculated, %: C 59.57; H 11.87; N 8.68; S 19.88. *M* 161. 309.

1-(Butylsulfanyl)-*N,N*-dimethylmethanamine (Ib). Yield 98% ($SmCl_3 \cdot 6H_2O$), n_D^{20} 1.4737, R_f 0.35. IR spectrum, cm^{-1}: 2958–2780, 1667, 1453, 1257, 1151, 1042, 786, 646. ^{1}H NMR spectrum, δ, ppm: 0.69 m (3H, CH_3), 1.16 m (2H, CH_2), 1.36 m (2H, CH_2), 1.99 br.s (6H, CH_3), 2.36 m (2H, CH_2), 3.67 br.s (2H, CH_2). ^{13}C NMR spectrum, δ, ppm: 13.42 s (C^{7}), 21.75 s (C^{6}), 32.38 s (C^{5}), 33.05 s (C^{4}), 42.32 s (C$^{8,8'}$), 64.32 s (C^{2}). Mass spectrum, *m/z* (I_{rel}, %): 147 (100) $[M]^+$, 90 $[M - (CH_3)_2NCH_2 + H]^+$, 58 $[M - C_4H_9S]^+$. Found, %: C 56.73; H 11.44; N 9.60; S 22.23. $C_7H_{17}NS$. Calculated, %: C 57.08; H 11.63; N 9.51; S 21.77. *M* 147.283.

1-(Heptylsulfanyl)-*N,N*-dimethylmethanamine (Ic). Yield 98% ($SmCl_3 \cdot 6H_2O$), n_D^{20} 1.4677, R_f 0.36. IR spectrum, cm^{-1}: 2926–2780, 1667, 1452, 1258, 1140, 1042, 816, 647. ^{1}H NMR spectrum, δ, ppm: 0.84 m (3H, CH_3), 1.31 m (8H, CH_2), 1.58 m (2H, CH_2), 2.23 br.s (6H, CH_3), 2.52 m (2H, CH_2), 3.87 br.s (2H, CH_2). ^{13}C NMR spectrum, δ, ppm: 14.01 s (C^{10}), 22.56 s (C^{9}), 28.84 s (C^{8}), 28.87 s (C^{7}), 30.10 s (C^{6}), 31.70 s (C^{5}), 33.77 s (C^{4}), 42.77 s (C$^{11,11'}$), 64.67 s (C^{2}). Mass spectrum, *m/z*: 189 $[M]^+$, 132 $[M - (CH_3)_2NCH_2 + H]^+$, 58 $[M - C_7H_{15}S]^+$. Found, %: C 63.32; H 12.35; N 8.16; S 16.17. $C_{10}H_{23}NS$. Calculated, %: C 63.43; H 12.24; N 7.40; S 16.93. *M* 189.362.

1-(Isopropylsulfanyl)-*N,N*-dimethylmethanamine (Id). Yield 95% ($SmCl_3 \cdot 6H_2O$), 98% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.6489, R_f 0.27. IR spectrum, cm^{-1}: 2972–2766, 1450, 1377, 1264, 1153, 1041, 816, 656. ^{1}H NMR spectrum, δ, ppm: 1.26 d (6H, CH_3, *J* 6.7 Hz), 2.44 br.s (6H, CH_3), 2.91 m (1H, CH, *J* 6.7 Hz), 3.71 br.s (2H, CH_2). ^{13}C NMR spectrum, δ, ppm: 24.04 s (C^{5,6}), 35.78 s (C^{4}), 42.87 s (C^{7,8}), 62.41 s (C^{2}). Found, %: C 54.32; H 11.05; N 10.06; S 24.57. $C_6H_{15}NS$. Calculated, %: C 54.08; H 11.35; N 10.51; S 24.06.

***1-(tert-*(Butylsulfanyl)-*N,N*-dimethylmethanamine (Ie).** Yield 97% ($SmCl_3 \cdot 6H_2O$), 95% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.6480, R_f 0.27. IR spectrum, cm^{-1}: 2973–2766, 1458, 1363, 1258, 1153, 1046, 817, 664. ^{1}H NMR spectrum, δ, ppm: 1.30 m (9H, CH_3), 2.25 m (6H, CH_3), 3.88 br.s (2H, CH_2). ^{13}C NMR spectrum, δ, ppm: 31.50 s (C^{5,6,7}), 41.77 s (C^{4}), 43.08 s (C^{8,9}), 59.94 s (C^{2}). Found, %: C 57.32; H 11.50; N 9.47; S 21.71. $C_7H_{17}NS$. Calculated, %: C 57.08; H 11.63; N 9.51; S 21.77.

***N,N*-Dimethyl-1-(phenylsulfanyl)methanamine (If).** Yield 88% ($SmCl_3 \cdot 6H_2O$), 90% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.6500, R_f 0.37. IR spectrum, cm^{-1}: 3071, 2973–2786, 1681, 1583, 1477–1437, 1254, 1127, 1046, 959, 742, 691, 622. ^{1}H NMR spectrum, δ, ppm: 2.34 br.s (6H, CH_3), 4.50 br.s (2H, CH_2), 7.29 t (3H, CH, *J* 7.2 Hz), 7.51 d (2H, CH, *J* 7.2 Hz). ^{13}C NMR spectrum, δ, ppm: 42.71 s (C^{10,11}), 69.01 s (C^{2}), 126.37 s (C^{7}), 128.94 s (C^{6,8}), 131.75 s (C^{5,9}), 138.17 s (C^{4}). Mass spectrum, *m/z* (I_{rel}, %): 167 (20) $[M]^+$, 91 (25) $[M - Ph + H]^+$, 58 (100) $[M - PhS + H]^+$. Found, %: C 64.52; H 7.95; N 8.27; S 19.26. $C_9H_{13}NS$. Calculated, %: C 64.62; H 7.83; N 8.37; S 19.17. *M* 167.272.

1-(Benzylsulfanyl)-*N,N*-dimethylmethanamine (Ig). Yield 84% ($SmCl_3 \cdot 6H_2O$), 84% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.5552, R_f 0.29. IR spectrum, cm^{-1}: 3061–3028, 2970–2775, 1602, 1494–1452, 1311, 1263, 1135, 1043, 815, 701, 641. ^{1}H NMR spectrum, δ, ppm: 2.33 s (6H, CH_3), 3.81 s (2H, CH_2), 3.88 br.s (2H, CH_2), 7.25 br.s (2H, CH), 7.36 br.s (3H, CH). ^{13}C NMR spectrum, δ, ppm: 36.94 s (C^{4}), 43.04 s (C^{11,12}), 63.21 s (C^{2}), 126.93 s (C^{8}), 128.24 s (C^{7,9}), 128.63 s (C^{6,10}), 139.00 s (C^{5}). Mass spectrum, *m/z* (I_{rel}, %): 181 (20) $[M]^+$, 91 (28) $[M - Bn + H]^+$, 58 (100) $[M - BnS + H]^+$. Found, %: C 66.21; H 8.33; N 7.77; S17.69. $C_{10}H_{15}NS$. Calculated, %: C 66.25; H 8.34; N 7.73; S 17.69. *M* 181.299.

1-(1,3-Benzothiazol-2-ylsulfanyl)-*N,N*-dimethylmethanamine (Ih). Yield 96% ($SmCl_3 \cdot 6H_2O$), mp 67–70°C, R_f 0.37. IR spectrum, cm^{-1}: 2923–2854, 1657–1587, 1462, 1406, 1330, 1275, 1134, 1061, 971, 723, 616. ^{1}H NMR spectrum, δ, ppm: 2.45 br.s (6H, CH_3), 4.93 t (2H, CH_2), 7.23–7.33 m (4H, CH). ^{13}C NMR spectrum, δ, ppm: 43.29 s ($C^{13,14}$), 68.88 s (C^{11}), 110.13 s (C^9), 110.87 s (C^6), 124.27 s (C^7), 124.87 s (C^8), 132.44 d (C^5), 147.13 s (C^4), 181.44 s (C^2). Mass spectrum, *m/z*: 223.682 $[M - H]^+$. Found, %: C 53.32; H 5.45; N 13.01; S 28.22. $C_{10}H_{12}N_2S_2$. Calculated, %: C 53.54; H 5.39; N 12.49; S 28.59. *M* 224.348.

1-(1,3-Benzoxazol-2-ylsulfanyl)-*N,N*-dimethylmethanamine (Ii). Yield 96% ($SmCl_3 \cdot 6H_2O$), mp 90–93°C, R_f 0.23. IR spectrum, cm^{-1}: 2925–2855, 1650–1581, 1462, 1377, 1258, 1127, 1031, 959, 719, 612. ^{1}H NMR spectrum, δ, ppm: 2.44 br.s (6H, CH_3), 5.05 t (2H, CH_2), 7.26–7.46 m (4H, CH). ^{13}C NMR spectrum, δ, ppm: 43.17 s ($C^{13,14}$), 67.65 s (C^{11}), 113.81 s (C^9), 120.88 s (C^6), 124.70 s (C^7), 126.78 s (C^8), 141.89 d (C^5), 162.97 s (C^4), 191.09 s (C^2). Mass spectrum, *m/z*: 207.646 $[M - H]^+$. Found, %: C 57.32; H 5.95; N 13.47; S 15.57. $C_{10}H_{12}N_2OS$. Calculated, %: C 57.67; H 5.81; N 13.45; S 15.40. *M* 208.281.

Aminomethylation of dithiols with *N,N,N′,N′*-tetramethylmethanediamine. In an argon atmosphere a mixture of 5 ml of chloroform, 0.5 mmol of catalyst $SmCl_3 \cdot 6H_2O$, 22 mmol of *N,N,N′,N′*-tetramethylmethanediamine, 10 mmol of an appropriate dithiol was stirred for 1.5 h at 60°C. Then from the reaction mixture the corresponding diaminodisulfides **II** were isolated by column chromatography on SiO_2.

***N*^{1},*N*^{1},*N*^{6},*N*^{6}-Tetramethyl-2,5-dithiahexane-1,6-diamine (IIa).** Yield 90% ($SmCl_3 \cdot 6H_2O$), 87% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.5032, R_f 0.10. IR spectrum, cm^{-1}: 2937–2778, 1681, 1451, 1314–1256, 1151, 1043, 902, 816, 638. ^{1}H NMR spectrum, δ, ppm: 2.22 br.s (12H, CH_3), 2.70 t (4H, CH_2), 3.88 br.s (4H, CH_2). ^{13}C, δ, ppm: 32.76 br.s ($C^{4,5}$), 42.77 s ($C^{9,9'}$), 64.91 br.s ($C^{2,7}$). Found, %: C 46.23; H 9.84; N 13.40; S 30.53. $C_8H_{20}N_2S_2$. Calculated, %: C 46.11; H 9.67; N 13.44; S 30.78.

***N*^{1},*N*^{1},*N*^{7},*N*^{7}-Tetramethyl-2,6-dithiaheptane-1,7-diamine (IIb).** Yield 86% ($SmCl_3 \cdot 6H_2O$), 83% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.4967, R_f 0.15. IR spectrum, cm^{-1}: 2937–2778, 1682, 1451, 1316–1249, 1151, 1043, 900, 836, 641. ^{1}H NMR spectrum, δ, ppm: 1.80 m (2H, CH_2), 2.23 br.s (12H, CH_3), 2.62 t (4H, CH_2), 3.88 br.s (4H, CH_2). ^{13}C NMR spectrum, δ, ppm: 29.35 s (C^5), 32.11 br.s ($C^{4,6}$), 42.57 s ($C^{10,10'}$), 64.46 br.s ($C^{2,8}$). Found, %: C 47.93; H 10.14; N 12.40; S 29.53. $C_9H_{22}N_2S_2$. Calculated, %: C 48.60; H 9.97; N 12.60; S 28.83.

***N*^{1},*N*^{1},*N*^{8},*N*^{8}-Tetramethyl-2,7-dithiaoctane-1,8-diamine (IIc).** Yield 85% ($SmCl_3 \cdot 6H_2O$), 72% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.4927, R_f 0.13. IR spectrum, cm^{-1}: 2937–2769, 1686, 1451, 1313–1259, 1164, 1042, 905, 816, 643. ^{1}H NMR spectrum, δ, ppm: 1.27 m (4H, CH_2), 1.82 br.s (12H, CH_3), 2.20 m (4H, CH_2), 3.46 m (4H, CH_2). ^{13}C NMR spectrum, δ, ppm: 25.65 s ($C^{5,6}$), 32.53 s ($C^{4,7}$), 42.37 s ($C^{11,11'}$), 64.06 s ($C^{2,9}$). Found, %: C 50.32; H 10.34; N 12.01; S 27.32. $C_{10}H_{24}N_2S_2$. Calculated, %: C 50.80; H 10.23; N 11.85; S 27.12.

***N*^{1},*N*^{1},*N*^{12},*N*^{12}-Tetramethyl-5,8-dioxa-2,11-dithiadodecane-1,12-diamine (IId).** Yield 81% ($SmCl_3 \cdot 6H_2O$), 77% ($FeCl_3 \cdot 6H_2O$), n_D^{20} 1.5135, R_f 0.13. IR spectrum, cm^{-1}: 2937–2770, 1680, 1450, 1315–1260, 1164, 1040, 905, 816, 645. ^{1}H NMR spectrum, δ, ppm: 2.27 br.s (12H, CH_3), 2.72 t (4H, CH_2), 3.58 t (4H, CH_2), 3.59 t (4H, CH_2), 3.96 br.s (4H, CH_2). ^{13}C NMR spectrum, δ, ppm: 32.64 s ($C^{4,11}$), 42.80 s ($C^{15,16,17,18}$), 65.13 s ($C^{2,13}$), 70.25 s ($C^{5,10}$), 71.58 s ($C^{7,8}$). Found, %: C 48.52; H 9.54; N 9.41; S 22.97. $C_{12}H_{28}N_2O_2S_2$. Calculated, %: C 48.61; H 9.52; N 9.45; S 21.63.

4,4′-Oxybis[(*N,N*-dimethyl)phenyl-1-sulfanylmethanamine] (IIe). Yield 80%, n_D^{20} 1.5478, R_f 0.13. IR spectrum, cm^{-1}: 2972–2860, 1657, 1580, 1483, 1313–1236, 1151, 1094, 905, 820, 724, 615. ^{1}H NMR spectrum, δ, ppm: 2.33 m (12H, CH_3), 4.43 s (4H, CH_2), 6.91 d (4H, CH, *J* 7.2 Hz), 7.45 d (4H, CH, *J* 7.2 Hz). ^{13}C NMR spectrum, δ, ppm: 36.76 s ($C^{11,11',12,12'}$), 42.37 s ($C^{11,11'}$), 63.94 s ($C^{9,9'}$), 113.51 d ($C^{4,4',6,6'}$), 126.60 d ($C^{5,5'}$), 126.82 d ($C^{3,3',7,7'}$), 149.93 d ($C^{2,2'}$). Found, %: C 61.32; H 7.24; N 8.01; S 18.97. $C_{18}H_{24}N_2S_2O$. Calculated, %: C 62.03; H 6.94; N 8.04; S 18.40.

Aminomethylation of thiols with *N,N,N′,N′*-tetramethylmethanediamine in the nmr tube in the spectrometer probe was carried out in a dynamic mode in two tubes. In the first tube 9.6×10^{-4} mol (100 mg) of $C_5H_{11}SH$, 9.8×10^{-4} mol (100 mg) of *N,N,N′,N′*-tetramethylmethanediamine, and 4.8×10^{-5} mol of $SmCl_3 \cdot 6H_2O$ in 0.25 ml $CDCl_3$ was mixed and then placed into the spectrometer probe for registering NMR spectra under the conditions of continuous registering at 298.1K. In the second tube the reaction was carried out in the absence of the catalyst under analogous conditions and the amounts of initial reagents.

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