

Aminomethylation of (ω -alkylthioalkyl)phenols

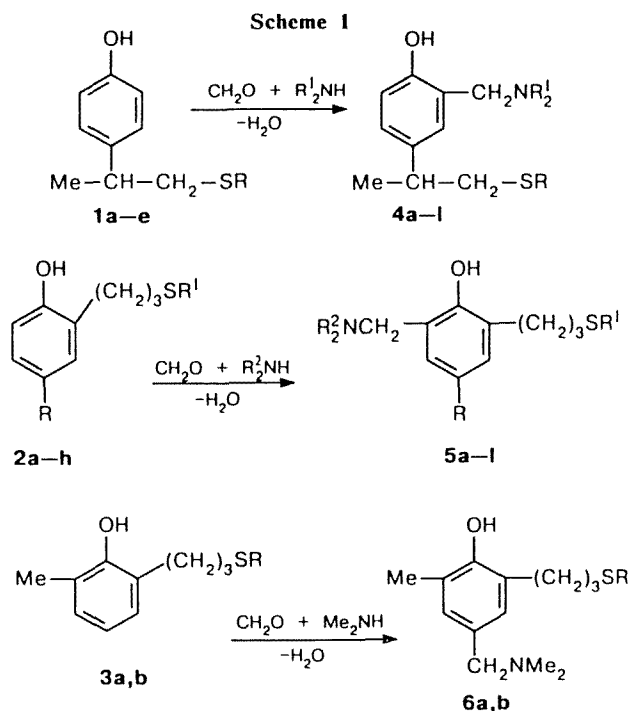
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The reactions of (ω -alkylthioalkyl)phenols with formaldehyde and secondary amines afforded the corresponding aminomethyl derivatives, in which the dimethylamino group may be replaced by the alkylthio group.

Key words: (ω -alkylthioalkyl)phenols, aminomethylation.

It may be assumed¹ that functionally substituted phenols, which simultaneously contain amino and disulfide groups, should exhibit good adhesive and anticorrosive properties.

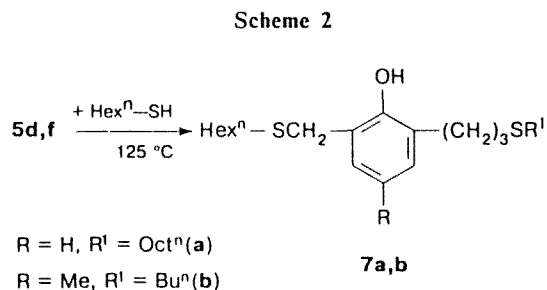


- 1,4:** $R^1 = \text{Me}$, $R = \text{Et}$ (**a**), Pr^n (**b**), Bu^n (**c**), Hex^n (**d**), Oct^n (**e**);
 $R = R^1 = \text{Et}$ (**f**);
 $R = \text{Et}$, $R^1_2 = (\text{CH}_2)_5$ (**g**), $(\text{CH}_2\text{CH}_2)_2\text{O}$ (**h**);
 $R = \text{Pr}^n$, $R^1 = \text{Et}$ (**i**), $\text{CH}_2\text{CH}_2\text{OH}$ (**j**);
 $R = \text{Pr}^n$, $R^1_2 = (\text{CH}_2)_5$ (**k**), $(\text{CH}_2\text{CH}_2)_2\text{O}$ (**l**)
- 2,5:** $R = \text{H}$, $R^2 = \text{Me}$, $R^1 = \text{Pr}^n$ (**a**), Bu^n (**b**), Hex^n (**c**), Oct^n (**d**);
 $R = R^2 = \text{Me}$, $R^1 = \text{Pr}^n$ (**e**), Bu^n (**f**), Hex^n (**g**), Oct^n (**h**);
 $R = \text{H}$, $R^1 = \text{Oct}^n$, $R^2 = \text{Et}$ (**i**), $\text{CH}_2\text{CH}_2\text{OH}$ (**j**),
 $R^2_2 = (\text{CH}_2)_5$ (**k**), $(\text{CH}_2\text{CH}_2)_2\text{O}$ (**l**)
- 3,6:** $R = \text{Pr}^n$ (**a**), Oct^n (**b**).

We have synthesized a series of new aminomethyl derivatives of (ω -alkylthioalkyl)phenols; the starting (ω -alkylthioalkyl)phenols **1a–e**, **2a–h**, and **3a,b** were obtained by the known procedures.² Aminomethylation was carried out in an aqueous solution under the action of equimolar amounts of amine and formaldehyde (Scheme 1).

After the reaction mixture was evaporated, the products of amination were isolated either by *in vacuo* distillation of the residue or by precipitation from ether with dry HCl as hydrochlorides followed by isolation of the base by treatment with aqueous ammonia.

With dimethylaminomethyl derivatives **5d,f** as an example, we have observed the exchange reaction of the dimethylamino group with the alkylthio group on heating with *n*-hexanthiol. Bis(alkylthioalkyl)phenols **7a,b** were obtained in 46–47 % yield (Scheme 2).



This reaction may be either a result of the direct substitution of the dimethylamino group under the action of the strong nucleophile RSH or the thermally initiated intermediate formation of the corresponding *o*-methylenequinone. The former variant seems to be more probable since the initial dimethylaminomethyl derivatives **5d,f** are distilled without decomposition at higher temperatures.

The composition and structure of all the products are confirmed by elemental analysis data and IR and ¹H NMR spectroscopy.

Experimental

^1H NMR spectra were recorded on a Tesla BS 487 C instrument (80 MHz) in CCl_4 or acetone- d_6 . Purity of the compounds was determined by TLC on Silufol UV-254 plates.

The starting alkenylphenols and phenol sulfides were synthesized by the known procedures.^{1,2}

4-(2-Ethylthio-1-methylethyl)-2-dimethylaminomethylphenol (4a). A mixture of 4-(2-ethylthio-1-methylethyl)phenol (**1a**) (9.8 g, 50 mmol), dimethylamine (2.3 g, 0.5 mmol), and formaldehyde (1.5 g, 0.05 mmol, 37 % aqueous solution) was stirred for 3 h at 25 °C, left for 16 h, and then heated for 1 h at 60 °C. Then the reaction mixture was concentrated, and the residue was distilled *in vacuo* to yield 10 g (80 %) of product **4a**, b.p. 146–151 °C (1 Torr), n_D^{20} 1.5537, d_4^{20} 1.05217. Found (%): C, 66.40; H, 9.09; N, 5.53; S, 12.65. $\text{C}_{14}\text{H}_{23}\text{NOS}$. Calculated (%): C, 66.42; H, 9.13; N, 5.50; S, 12.63. ^1H NMR, δ : 1.04 (t, 3 H, CH_3CH_2); 1.17 (d, 3 H, CH_3CH); 2.11 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.21 (q, 2 H, CH_2CH_3); 2.59 (d, 2 H, SCH_2CH); 2.66 (m, 1 H, CH); 3.46 (s, 2 H, CH_2N); 6.49–6.93 (m, 3 H, C_6H_3); 8.49 (br.s, 1 H, OH).

4-(1-Methyl-2-propylthioethyl)-2-dimethylaminomethylphenol (4b) was synthesized similarly to **4a** in 80 % yield, b.p. 155–160 °C (1 Torr), n_D^{20} 1.5440, d_4^{20} 1.04126. Found (%): C, 67.27; H, 9.12; N, 5.11; S, 11.83. $\text{C}_{15}\text{H}_{25}\text{NOS}$. Calculated (%): C, 67.42; H, 9.36; N, 5.42; S, 11.99. ^1H NMR, δ : 0.85 (t, 3 H, CH_3CH_2); 1.19 (d, 3 H, CH_3CH); 1.64 (m, 2 H, CH_2); 2.15 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.28 (t, 2 H, SCH_2CH_2); 2.53 (d, 2 H, CH_2CH); 2.61 (m, 1 H, CHCH_3); 3.45 (s, 2 H, CH_2N); 6.50–6.81 (m, 3 H, C_6H_3); 9.40 (br.s, 1 H, OH).

4-(2-Butylthio-1-methylethyl)-2-dimethylaminomethylphenol (4c) was synthesized similarly to **4a** in 78.3 % yield, n_D^{20} 1.5260, d_4^{20} 1.0367. Found (%): C, 68.32; H, 9.09; N, 4.98; S, 11.38. $\text{C}_{16}\text{H}_{27}\text{NOS}$. Calculated (%): C, 68.40; H, 9.20; N, 4.90; S, 11.40. ^1H NMR, δ : 0.85 (t, 3 H, CH_3CH_2); 1.18 (d, 3 H, CH_3CH); 1.64 (m, 2 H, CH_2); 2.11 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.21 (q, 2 H, CH_2CH_3); 2.28 (t, 1 H, SCH_2CH_2); 2.53 (d, 2 H, CH_2CH); 2.61 (m, 1 H, CHCH_3); 3.45 (s, 2 H, CH_2N); 6.45–6.93 (m, 3 H, C_6H_3); 8.49 (br.s, 1 H, OH).

4-(2-Hexylthio-1-methylethyl)-2-dimethylaminomethylphenol (4d) was synthesized similarly to **4a** in 76 % yield, n_D^{20} 1.5291, d_4^{20} 0.9834. Found (%): C, 69.9; H, 10.03; N, 4.75; S, 10.85. $\text{C}_{18}\text{H}_{31}\text{NOS}$. Calculated (%): C, 70.10; H, 10.0; N, 4.80; S, 10.90. ^1H NMR, δ : 1.18 (d, 3 H, CH_3CH); 1.64 (m, 2 H, CH_2); 2.11 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.59 (d, 2 H, SCH_2CH); 3.46 (s, 2 H, CH_2N); 6.49–6.93 (m, 3 H, C_6H_3); 8.49 (br.s, 1 H, OH).

4-(1-Methyl-2-octylthioethyl)-2-dimethylaminomethylphenol (4e) was synthesized similarly to **4a** in 67 % yield, n_D^{20} 1.5137, d_4^{20} 0.9293. Found (%): C, 70.65; H, 10.25; N, 4.28; S, 9.98. $\text{C}_{20}\text{H}_{35}\text{NOS}$. Calculated (%): C, 70.95; H, 10.21; N, 4.32; S, 9.90. ^1H NMR, δ : 1.18 (d, 3 H, CH_3CH); 1.64 (m, 2 H, CH_2); 2.11 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.57 (d, 2 H, SCH_2CH); 2.59 (d, 2 H, SCH_2CH); 3.45 (s, 2 H, CH_2N); 6.49–6.93 (m, 3 H, C_6H_3); 8.49 (br.s, 1 H, OH).

4-(2-Ethylthio-1-methylethyl)-2-diethylaminomethylphenol (4f). 2-Ethylthio-1-methylethylphenol (**1a**) (9.8 g, 50 mmol) was added to a mixture of diethylamine (3.7 g, 50 mmol) and formaldehyde (1.5 g, 50 mmol, 37 % aqueous solution) with stirring, and the mixture was heated at 70–73 °C for 4 h. The mixture was then cooled and extracted with ether, and the extract was washed with water and dried with CaCl_2 . Dry HCl was passed through the residue, and the crystals were filtered

off, washed with ether, treated with 25 % aqueous ammonia (200 mL), and extracted with ether. The extract was dried with CaCl_2 , and ether was distilled off to yield 13 g (86.4 %) of product **4f**, n_D^{20} 1.5644, d_4^{20} 0.96334. Found (%): C, 68.51; H, 9.43; N, 5.01; S, 11.48. $\text{C}_{16}\text{H}_{27}\text{NOS}$. Calculated (%): C, 68.33; H, 9.61; N, 4.98; S, 11.39. ^1H NMR, δ : 1.18 (d, 3 H, CH_3CH_2); 1.48 (d, 3 H, CH_3CH); 2.51 (q, 2 H, SCH_2CH_3); 2.67 (q, 4 H, NCH_2CH_3); 2.80 (d, 2 H, SCH_2CH); 2.94 (m, 1 H, CH); 3.79 (s, 2 H, CH_2N); 6.80 and 7.04 (both m, 3 H, C_6H_3); 9.99 (br.s, 1 H, OH).

4-(2-Ethylthio-1-methylethyl)-2-piperidinomethylphenol (4g) was synthesized similarly to **4f** in 82 % yield, n_D^{20} 1.5115, d_4^{20} 0.9795. Found (%): C, 70.10; H, 9.15; N, 4.80; S, 10.65. $\text{C}_{17}\text{H}_{27}\text{NOS}$. Calculated (%): C, 69.62; H, 9.21; N, 4.78; S, 10.92. ^1H NMR, δ : 1.40 (t, 3 H, CH_3CH_2); 1.53 (d, 3 H, CH_3CH); 1.75 (m, 6 H, $(\text{CH}_2)_3$); 2.56 (q, 2 H, SCH_2CH_3); 2.65 (m, 4 H, CH_2NCH_2); 2.86 (d, 2 H, CH_2S); 3.00 (m, 1 H, CH); 3.78 (s, 2 H, CH_2N); 6.85 and 7.15 (both m, 3 H, C_6H_3); 9.95 (br.s, 1 H, OH).

4-(2-Ethylthio-1-methylethyl)-2-morpholinomethylphenol (4h) was synthesized similarly to **4f** in 81 % yield, n_D^{20} 1.4910, d_4^{20} 1.0316. Found (%): C, 65.13; H, 8.50; N, 4.73; S, 10.90. $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{S}$. Calculated (%): C, 65.08; H, 8.47; N, 4.75; S, 10.85. ^1H NMR, δ : 1.29 (t, 3 H, CH_3CH_2); 1.44 (d, 3 H, CH_3CH); 2.53 (q, 2 H, CH_2CH_3); 2.58 (t, 4 H, CH_2NCH_2); 2.80 (d, 2 H, CH_2CH); 2.95 (m, 1 H, CH); 3.71 (m, 6 H, CH_2OCH_2 and CH_2N); 6.88 and 7.14 (both m, 3 H, C_6H_3); 7.88 (br.s, 1 H, OH).

4-(1-Methyl-2-propylthioethyl)-2-diethylaminomethylphenol (4i) was synthesized similarly to **4f** in 88.29 % yield, n_D^{20} 1.5425, d_4^{20} 0.9822. Found (%): C, 69.18; H, 9.79; N, 4.71; S, 10.88. $\text{C}_{17}\text{H}_{29}\text{NOS}$. Calculated (%): C, 69.15; H, 9.83; N, 4.74; S, 10.85. ^1H NMR, δ : 1.19 (t, 3 H, CH_3CH_2); 1.23 (t, 3 H, $\text{CH}_3\text{CH}_2\text{N}$); 1.81 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$); 2.28 (d, 2 H, SCH_2CH); 2.50 (m, 2 H, SCH_2CH_3); 2.67 (q, 4 H, NCH_2CH_3); 2.95 (m, 1 H, CH); 3.85 (s, 2 H, CH_2N); 6.80 and 7.03 (both m, 3 H, C_6H_3); 9.95 (br.s, 1 H, OH).

Bis(2-hydroxyethyl)-4-(1-methyl-2-propylthioethyl)phenol (4j) was synthesized similarly to **4f** in 70 % yield, n_D^{20} 1.5455, d_4^{20} 0.1196. Found (%): C, 69.20; H, 9.90; N, 4.75; S, 10.80. $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{S}$. Calculated (%): C, 69.15; H, 9.83; N, 4.71; S, 10.85. ^1H NMR, δ : 1.19 (t, 3 H, CH_3CH_2); 1.48 (d, 3 H, CH_3CH); 1.81 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$); 2.26 (t, 2 H, SCH_2CH_2); 2.54 (t, 4 H, CH_2N); 2.56 (d, 2 H, SCH_2CH); 2.95 (m, 1 H, CH); 3.47 (s, 2 H, CH_2N); 3.55 (t, 4 H, 2 CH_2O); 6.80 and 7.03 (both m, 3 H, C_6H_3); 9.93 (br.s, 1 H, OH).

4-(1-Methyl-2-propylthioethyl)-2-piperidinomethylphenol (4k) was synthesized similarly to **4f** in 87.29 % yield, n_D^{20} 1.5395, d_4^{20} 1.0034. Found (%): C, 70.33; H, 9.41; N, 4.60; S, 10.40. $\text{C}_{18}\text{H}_{29}\text{NOS}$. Calculated (%): C, 70.35; H, 9.44; N, 4.56; S, 10.42. ^1H NMR, δ : 1.20 (t, 3 H, CH_3CH_2); 1.55 (d, 3 H, CH_3CH); 1.83 (m, 6 H, $(\text{CH}_2)_3$); 2.63 (q, 2 H, CH_2CH_3); 2.71 (m, 4 H, CH_2NCH_2); 2.88 (d, 2 H, CH_2S); 3.05 (m, 1 H, CH); 3.88 (s, 2 H, CH_2N); 6.85 and 7.15 (both m, 3 H, C_6H_3); 9.98 (br.s, 1 H, OH).

4-(1-Methyl-2-propylthioethyl)-2-morpholinomethylphenol (4l) was synthesized similarly to **4f** in 77.7 % yield, n_D^{20} 1.5245, d_4^{20} 1.0155. Found (%): C, 66.00; H, 8.75; N, 4.55; S, 10.39. $\text{C}_{17}\text{H}_{27}\text{NO}_2\text{S}$. Calculated (%): C, 66.01; H, 8.73; N, 4.53; S, 10.35. ^1H NMR, δ : 1.16 (t, 3 H, CH_3CH_2); 1.50 (d, 3 H, CH_3CH); 1.79 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$); 2.51 (q, 2 H, CH_2CH_3); 2.59 (t, 4 H, CH_2NCH_2); 2.83 (d, 2 H, CH_2CH); 2.97 (m, 1 H, CH); 3.79 (m, 6 H, CH_2OCH_2 and NCH_2Ar); 6.87 and 7.16 (both m, 3 H, C_6H_3); 8.88 (br.s, 1 H, OH).

2-Dimethylaminomethyl-6-(3-propylthiopropyl)phenol (5a).

2-(1-Methyl-3-propylthioethyl)phenol **2a** (21.0 g, 0.1 mol) was gradually added to a mixture of dimethylamine (4.5 g, 0.1 mol, 33 % aqueous solution) and formaldehyde (3 g, 0.1 mol, 37 % aqueous solution) with stirring at 20–25 °C. The mixture was stirred for 4 h at 70–75 °C, cooled, and extracted with ether. The extract was washed with water and washed with CaCl_2 . Dry HCl was passed through the ethereal solution, and the hydrochloride formed was filtered off, washed with water, and decomposed with aqueous ammonia to afford 20.48 g (82.4 %) of product **5a**, b.p. 140–143 °C (10.5 Torr), n_D^{20} 1.5320, d_4^{20} 1.0011. Found (%): C, 67.03; H, 9.1; N, 5.17; S, 11.99. $\text{C}_{15}\text{H}_{25}\text{NOS}$. Calculated (%): C, 67.41; H, 9.36; N, 5.24; S, 11.99. ^1H NMR, δ : 0.89 (t, 3 H, CH_3CH_2); 1.49 (m, 2 H, CH_2CH_3); 1.78 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.19 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.26 (t, 2 H, CH_2S); 2.36 (t, 2 H, CH_2S); 2.56 (t, 2 H, CH_2Ar); 3.45 (s, 2 H, CH_2); 6.56 (m, 3 H, C_6H_3); 10.09 (br.s, 1 H, OH).

6-(3-Butylthiopropyl)-2-dimethylaminomethylphenol (5b)

was synthesized similarly to **5a** in 78.3 % yield, n_D^{20} 1.5235, d_4^{20} 0.98603. Found (%): C, 67.89; H, 9.14; N, 4.47; S, 11.03. $\text{C}_{16}\text{H}_{27}\text{NOS}$. Calculated (%): C, 68.33; H, 9.61; N, 4.98; S, 11.39. ^1H NMR, δ : 0.84 (t, 3 H, CH_3CH_2); 1.38 (m, 4 H, $(\text{CH}_2)_2$); 1.80 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.18 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.28 (t, 2 H, CH_2S); 2.38 (t, 2 H, CH_2S); 2.58 (t, 2 H, CH_2Ar); 3.45 (s, 2 H, CH_2N); 6.60 (m, 3 H, C_6H_3); 10.05 (br.s, 1 H, OH).

6-(3-Hexylthiopropyl)-2-dimethylaminomethylphenol (5c)

was synthesized similarly to **5a** in 76.7 % yield, n_D^{20} 1.5225, d_4^{20} 0.98324. Found (%): C, 69.47; H, 9.84; N, 4.11; S, 10.01. $\text{C}_{18}\text{H}_{31}\text{NOS}$. Calculated (%): C, 69.90; H, 10.03; N, 4.53; S, 10.36. ^1H NMR, δ : 0.85 (t, 3 H, CH_3CH_2); 1.25 (m, 8 H, $(\text{CH}_2)_4$); 1.79 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.20 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.25 (t, 2 H, CH_2S); 2.36 (t, 2 H, CH_2S); 2.58 (t, 2 H, CH_2Ar); 3.45 (s, 2 H, CH_2N); 6.58 (m, 3 H, C_6H_3); 9.90 (br.s, 1 H, OH).

2-Dimethylaminomethyl-6-(3-octylthiopropyl)phenol (5d)

was synthesized similarly to **5a** in 75 % yield, n_D^{20} 1.5180, d_4^{20} 0.96731. Found (%): C, 70.87; H, 10.01; N, 3.68; S, 9.43. $\text{C}_{20}\text{H}_{35}\text{NOS}$. Calculated (%): C, 71.22; H, 10.39; N, 4.15; S, 9.50. ^1H NMR, δ : 0.81 (t, 3 H, CH_3CH_2); 1.18 (m, 12 H, $(\text{CH}_2)_6$); 1.74 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.18 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.25 (t, 2 H, CH_2S); 2.35 (t, 2 H, CH_2S); 2.56 (t, 2 H, CH_2Ar); 3.44 (s, 2 H, CH_2N); 6.56 (m, 3 H, C_6H_3); 10.01 (br.s, 1 H, OH).

4-Methyl-2-dimethylaminomethyl-6-(3-propylthiopropyl)phenol (5e) was synthesized similarly to **5a** in 79.9 % yield, n_D^{20} 1.5290, d_4^{20} 0.9986. Found (%): C, 67.87; H, 9.47; N, 4.54; S, 10.94. $\text{C}_{16}\text{H}_{27}\text{NOS}$. Calculated (%): C, 68.33; H, 9.61; N, 4.98; S, 10.94. ^1H NMR, δ : 0.89 (t, 3 H, CH_3CH_2); 1.48 (m, 2 H, CH_2CH_3); 1.71 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.06 (s, 3 H, CH_3Ar); 2.14 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.24 (t, 2 H, CH_2S); 2.32 (t, 2 H, CH_2S); 2.51 (t, 2 H, CH_2Ar); 3.36 (s, 2 H, CH_2N); 6.51 (2 H, spectrum of AB type, C_6H_2); 9.81 (br.s, 1 H, OH).

6-(3-Butylthiopropyl)-4-methyl-2-dimethylaminomethylphenol (5f) was synthesized similarly to **5a** in 77.3 % yield, n_D^{20} 1.5275, d_4^{20} 0.9826. Found (%): C, 68.73; H, 9.54; N, 4.21; S, 10.57. $\text{C}_{17}\text{H}_{29}\text{NOS}$. Calculated (%): C, 69.15; H, 9.83; N, 4.75; S, 10.85. ^1H NMR, δ : 0.83 (t, 3 H, CH_3CH_2); 1.39 (m, 4 H, $(\text{CH}_2)_2$); 1.71 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.06 (s, 3 H, CH_3Ar); 2.16 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.26 (t, 2 H, CH_2S); 2.36 (t, 2 H, CH_2S); 2.51 (t, 2 H, CH_2Ar); 3.36 (s, 2 H, CH_2N); 6.51 (2 H, spectrum of AB type, C_6H_2); 9.78 (br.s, 1 H, OH).

6-(3-Hexylthiopropyl)-4-methyl-2-dimethylaminomethylphenol (5g) was synthesized similarly to **5a** in 74 % yield, n_D^{20}

1.5285, d_4^{20} 0.9790. Found (%): C, 70.04; H, 9.83; N, 4.11; S, 9.78. $\text{C}_{19}\text{H}_{33}\text{NOS}$. Calculated (%): C, 70.59; H, 10.22; N, 4.33; S, 9.01. ^1H NMR, δ : 0.81 (t, 3 H, CH_3CH_2); 1.23 (m, 8 H, $(\text{CH}_2)_4$); 1.71 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.06 (s, 3 H, CH_3Ar); 2.16 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.26 (t, 2 H, CH_2S); 2.35 (t, 2 H, CH_2S); 2.51 (t, 2 H, CH_2Ar); 3.38 (s, 2 H, CH_2N); 6.51 (2 H, spectrum of AB type, C_6H_2); 9.76 (br.s, 1 H, OH).

4-Methyl-2-dimethylaminomethyl-6-(3-octylthiopropyl)phenol (5h) was synthesized similarly to **5a** in 69.2 % yield, n_D^{20} 1.5155, d_4^{20} 0.95215. Found (%): C, 71.54; H, 10.32; N, 3.99; S, 9.12. $\text{C}_{21}\text{H}_{37}\text{NOS}$. Calculated (%): C, 71.79; H, 10.54; N, 3.99; S, 9.12. ^1H NMR, δ : 0.80 (t, 3 H, CH_3); 1.16 (m, 12 H, $(\text{CH}_2)_6$); 1.75 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.05 (s, 3 H, CH_3Ar); 2.15 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.25 (t, 2 H, CH_2S); 2.35 (t, 2 H, CH_2S); 2.51 (t, 2 H, CH_2Ar); 3.38 (s, 2 H, NCH_2Ar); 6.54 (2 H, spectrum of AB type, C_6H_2); 9.90 (br.s, 1 H, OH).

2-Diethylaminomethyl-6-(3-octylthiopropyl)phenol (5i) was synthesized similarly to **5a** in 62.8 % yield, n_D^{20} 1.5159, d_4^{20} 0.9475. Found (%): C, 72.10; H, 10.47; N, 3.47; S, 8.11. $\text{C}_{22}\text{H}_{39}\text{NOS}$. Calculated (%): C, 72.33; H, 10.68; N, 3.84; S, 8.77. ^1H NMR, δ : 0.89 (t, 3 H, CH_3); 0.99 (t, 6 H, $(\text{CH}_3\text{CH}_2)_2\text{N}$); 1.19 (m, 12 H, $(\text{CH}_2)_6$); 1.81 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.38 (m, 8 H, 2 CH_2S , 2 CH_2N); 2.58 (t, 2 H, CH_2Ar); 3.54 (s, 2 H, NCH_2Ar); 6.56 (m, 3 H, C_6H_3); 10.39 (br.s, 1 H, OH).

2-Bis(2-hydroxyethyl)aminomethyl-6-(3-octylthiopropyl)phenol (5j) was synthesized similarly to **5a** in 62.6 % yield, n_D^{20} 1.5275, d_4^{20} 1.0601. Found (%): C, 66.44; H, 9.67; N, 3.37; S, 7.94. $\text{C}_{22}\text{H}_{39}\text{NOS}_3$. Calculated (%): C, 66.5; H, 9.82; N, 3.53; S, 8.06. ^1H NMR, δ : 0.80 (t, 3 H, CH_3); 1.15 (m, 12 H, $(\text{CH}_2)_6$); 1.72 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.35 (m, 8 H, 2 CH_2S , 2 CH_2N); 2.54 (t, 2 H, CH_2Ar); 3.47 (s, 2 H, NCH_2Ar); 3.55 (t, 4 H, 2 CH_2O); 6.58 (m, 3 H, C_6H_3); 12.82 (br.s, 3 H, 3 OH).

6-(3-Octylthiopropyl)-2-piperidinomethylphenol (5k) was synthesized similarly to **5a** in 65 % yield, n_D^{20} 1.5144, d_4^{20} 0.9908. Found (%): C, 73.07; H, 10.14; N, 3.58; S, 7.94. $\text{C}_{23}\text{H}_{39}\text{NOS}$. Calculated (%): C, 73.21; H, 10.35; N, 3.71; S, 8.49. ^1H NMR, δ : 0.80 (t, 3 H, CH_3); 1.19 (m, 12 H, $(\text{CH}_2)_6$); 1.45 (m, 6 H, $(\text{CH}_2)_3$); 1.77 (t, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.35 (m, 8 H, 2 CH_2S , 2 CH_2N); 2.53 (t, 2 H, CH_2Ar); 3.48 (s, 2 H, NCH_2Ar); 6.58 (m, 3 H, C_6H_3); 9.50 (br.s, 1 H, OH).

2-Morpholinomethyl-6-(3-octylthiopropyl)phenol (5l) was synthesized similarly to **5a** in 73.26 % yield, n_D^{20} 1.5127, d_4^{20} 1.0197. Found (%): C, 69.27; H, 9.44; N, 3.53; S, 8.08. $\text{C}_{22}\text{H}_{37}\text{NOS}_2$. Calculated (%): C, 69.66; H, 9.76; N, 3.69; S, 8.44. ^1H NMR, δ : 0.79 (t, 3 H, CH_3CH_2); 1.15 (m, 12 H, $(\text{CH}_2)_6$); 1.71 (t, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.34 (m, 8 H, 2 CH_2S , 2 CH_2N); 2.56 (t, 2 H, CH_2Ar); 3.48 (m, 6 H, NCH_2Ar , 2 CH_2O); 6.56 (m, 3 H, C_6H_3); 9.51 (br.s, 1 H, OH).

2-Methyl-4-dimethylaminomethyl-6-(3-propylthiopropyl)phenol (6a) was synthesized similarly to **5a** in 48.2 % yield, n_D^{20} 1.5295, d_4^{20} 0.9979. Found (%): C, 67.95; H, 9.61; N, 5.00; S, 11.30. $\text{C}_{16}\text{H}_{27}\text{NOS}$. Calculated (%): C, 68.33; H, 9.61; N, 4.98; S, 11.39. ^1H NMR, δ : 0.83 (t, 3 H, CH_3); 1.39 (m, 4 H, $(\text{CH}_2)_2$); 1.71 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.06 (s, 3 H, CH_3Ar); 2.16 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.26 (t, 2 H, CH_2S); 2.36 (t, 2 H, CH_2S); 2.51 (t, 2 H, CH_2Ar); 3.36 (s, 2 H, NCH_2Ar); 6.51 (s, 2 H, C_6H_2); 6.95 (br.s, 1 H, OH).

2-Methyl-4-dimethylaminomethyl-6-(3-octylthiopropyl)phenol (6b) was synthesized similarly to **5a** in 41.20 % yield, n_D^{20} 1.5290, d_4^{20} 0.9822. Found (%): C, 71.68; H, 10.49; N, 3.92; S, 9.23. $\text{C}_{21}\text{H}_{37}\text{NOS}$. Calculated (%): C, 71.73; H, 10.54;

N, 3.99; S, 9.12. ^1H NMR, δ : 0.81 (t, 3 H, CH_3); 1.19 (m, 12 H, 6 CH_2); 1.69 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 2.04 (s, 3 H, CH_3Ar); 2.12 (s, 6 H, $(\text{CH}_3)_2\text{N}$); 2.26 (t, 2 H, CH_2S); 2.36 (t, 2 H, CH_2S); 2.50 (t, 2 H, CH_2Ar); 3.29 (s, 2 H, NCH_2Ar); 6.69 (s, 2 H, C_6H_2); 6.36 (br.s, 1 H, OH).

2-Hexylthiomethyl-6-(3-octylthiopropyl)phenol (7a). A mixture of compound **5d** (29.5 g, 0.1 mol) and hexanethiol (13.2 g, 0.1 mol) was stirred for 10 h at 125 °C. The mixture was then cooled and poured into benzene (150 mL), and dry HCl was passed through the solution. The salt of the non-reacted initial amine **5d** was washed off with water, the benzene solution was dried with CaCl_2 , concentrated, and fractionated to yield 17.95 g (47.0 %) of product **7a**, b.p. 206–209 °C (1 Torr), n_D^{20} 1.5220, d_4^{20} 0.9352. Found (%): C, 68.94; H, 9.85; S, 16.58. $\text{C}_{24}\text{H}_{36}\text{SO}_2$. Calculated (%): C, 68.94; H, 9.95; S, 16.75. ^1H NMR, δ : 0.80 (t, 3 H, CH_3); 0.83 (t, 3 H, CH_3); 1.18 (m, 10 H, $(\text{CH}_2)_5$); 1.74 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 1.84 (m, 4 H, $(\text{CH}_2)_2$); 2.09 (s, 3 H, CH_3Ar); 2.28 (t, 2 H, CH_2S); 2.36 (t, 4 H, 2 SCH_2); 2.54 (t, 2 H, CH_2Ar); 3.59 (s, 2 H, SCH_2Ar); 6.59 (2 H, spectrum of AB type, C_6H_2); 6.46 (br.s, 1 H, OH).

6-(3-Butylthiopropyl)-2-hexylthiomethyl-4-methylphenol (7b) was synthesized similarly to **7a** in 46.2 % yield, b.p. 200–202 °C (1 Torr), n_D^{20} 1.5019, d_4^{20} 0.91034. Found (%): C, 70.44; H, 10.09; S, 14.97. $\text{C}_{21}\text{H}_{30}\text{S}_2\text{O}$. Calculated (%): C, 70.75; H, 10.38; S, 15.09. ^1H NMR, δ : 0.80 (t, 3 H, CH_3); 0.83 (t, 3 H, CH_3); 1.18 (m, 10 H, $(\text{CH}_2)_5$); 1.74 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2$); 1.84 (m, 4 H, $(\text{CH}_2)_2$); 2.09 (s, 3 H, CH_3Ar); 2.28 (t, 2 H, CH_2S); 2.36 (t, 4 H, 2 SCH_2); 2.54 (t, 2 H, CH_2Ar); 3.59 (s, 2 H, SCH_2Ar); 6.59 (2 H, spectrum of AB type, C_6H_2); 6.06 (br.s, 1 H, OH).

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