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Cyclocondensation of Unsymmetrical Perfluoroalkyl-Substituted β-Diketones with Urea, Thiourea, and Guanidine

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Abstract—The reactions of unsymmetrical perfluoroalkyl-substituted β-diketones with guanidine, urea, and thiourea gave the corresponding 2-amino-, 2-hydroxy-, and 2-sulfanyl-6-perfluoroalkyl-4-methylpyrimidines.

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The subjects of the present study are fluorine-containing pyrimidine derivatives which constitute a new class of potential biologically active substances and compounds possessing anticorrosion properties. Despite the fact that some fluoropyrimidines have long been known [1–11] and have found wide applpication (e.g., 5-fluorouracil and Ftorafur), methods of synthesis and chemical properties of fluorine-containing nitrogen heterocycles have been studied fairly poorly, so that relevant studies remain strongly desirable. Taking the above stated into account, the goal of the present work was to develop an acceptable procedure for the synthesis of functionally substituted perfluoroalkylpyrimidines.

Nitrogen-containing heterorings can be built up via intramolecular dehydrogenation, dehydration, and deamination, as well as by intermolecular condensations of amino, imino, carbonyl, and hydroxy compounds [1–11]. One of the main methods for the synthesis of pyrimidine derivatives is based on cyclocondensation of β-dicarbonyl compounds with urea and its derivatives. We now propose a procedure on the basis of reactions of perfluoroalkyl-substituted β-diketones with guanidine, urea, and thiourea. Perfluorinated 1,3-diketones can be obtained by different methods, such as Claisen condensation [12–14], Meerwein reaction [15], and reaction of fluorinated olefins with acid fluorides under pressure in the presence of antimony pentafluoride at 20°C (ratio RCOF–SbF_5 6:1, yield 40%) [16]. We synthesized fluorinated 1,3-diketones by one-step procedure according to Meerwein [15] using large-scale intermediate products, perfluoroacyl fluorides $C_6F_{13}COF$, $C_8F_{17}COF$, and $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)COF$ (n = 1, 2, 3, 9), as starting compounds. The reactions were performed by treatment of perfluorinated carboxylic acid fluorides with 3–5 equiv of acetone in the presence of sodium fluoride as hydrogen fluoride acceptor on heating at the boiling point over a period of 10–15 h. As a result, we obtained the corresponding unsymmetrical perfluoroalkyl-containing β-diketones **Ia**–**If** (Scheme 1).

Scheme 1.

Ia–If

$R_F = C_6F_{13}$ (**a**), C_8F_{17} (**b**), $C_3F_7OCF(CF_3)$ (**c**), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (**d**), $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$ (**e**), $C_3F_7O[CF(CF_3)CF_2O]_9CF(CF_3)$ (**f**).

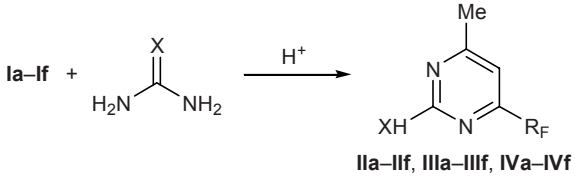
The structure of β-diketones **Ia**–**If** was confirmed by the IR spectra and elemental analyses. The IR spectra of **Ia**–**If** contained absorption bands in the region 3450–2985 cm^{-1} due to stretching vibrations of C–H bonds, bands at 1350–950 cm^{-1} were attributed to stretching vibrations of C–F and C–O (ether) bonds, and ketone carbonyl bands were observed at 1780–1770 cm^{-1}, in keeping with published data [17]. The spectra of all compounds **Ia**–**If** lacked absorption in the region 1890–1880 cm^{-1}, which is typical of initial perfluoroacyl fluorides.

Condensations of 1,3-diketones or their analogs with various guanidine and urea derivatives are widely used for the synthesis of pyrimidine compounds [1–11]. For example, fusion of guanidine carbonate with 1,1,1-trifluoropentane-2,4-dione derivatives (140–150°C, 1 h) was reported to give 4-substituted 2-amino-

pyrimidines (yield 79–90%) [4], cyclization of ethylguanidine with 1,3-diketones in a mixture of diethyl ether with ethanol at room temperature (14 h) gave 6-trifluoromethyl- and 6-heptafluoropropylpyrimidines (25–63%) [5], 4-trifluoromethylpyrimidine derivatives were synthesized by reaction of fluorinated β-diketones with 4-tolylguanidine (90–115°C, 8–12 h) [6] and *N*-(2-hydroxyethyl)-*N*-methylguanidine sulfate [7] in the presence of sodium carbonate, while guanidine carbonate gave rise to 6-perfluoroalkylpyrimidines (ethanol, 10–14 h, yield 73–82%) [8, 9]. Kucerovy et al. [10] reported on the synthesis of mono- and bis(trifluoromethyl)- and *p*-fluorophenyl-substituted 2-aminopyrimidines by condensation of aminoguanidine derivatives with various fluorine-containing β-diketones (12 h, yield 54–82%). Urea, *N*-methylurea, *N*,*N*′-dimethylurea, and thiourea reacted with 1,1,1-trifluoropentane-2,4-dione in the presence of hydrochloric acid to produce the corresponding 2-hydroxy- and 2-sulfanylpyrimidine derivatives [11]. Analysis of published data [1–11] led us to select acid-catalyzed cyclocondensation of β-dicarbonyl compounds with urea and its analogs for the synthesis of the desired fluorine-containing pyrimidine derivatives, taking into account relatively mild conditions of the process and high yield.

The reactions were carried out in a polar solvent (propan-2-ol) using equimolar amounts of β-diketone **Ia**–**If** and guanidine carbonate, urea, or thiourea in the presence of hydrochloric acid on heating (70–80°C; 3–5 h). As a result, we obtained 6-perfluoroalkyl-substituted 4-methylpyrimidines **IIa**–**IIf**, **IIIa**–**IIIf**, and **IVa**–**IVf**, respectively, in 68–95% yield (Scheme 2). Compounds **IIa**–**IVa** were also obtained in propan-2-ol at room temperature, but the reaction time was three days, and the yields of **IIa**, **IIIa**, and **IVa** were 68, 72, and 72%, respectively. The progress of the reactions was monitored by thin-layer chromatography, following disappearance of the initial diketone. In no case condensation products at only one carbonyl group were detected.

Scheme 2.



II, X = NH; **III**, X = O; **IV**, X = S; $R_F = C_6F_{13}$ (**a**), C_8F_{17} (**b**), $C_3F_7OCF(CF_3)$ (**c**), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (**d**), $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$ (**e**), $C_3F_7O[CF(CF_3)CF_2O]_9CF(CF_3)$ (**f**).

Compounds **II**–**IV** were isolated by neutralization of the reaction mixture with a solution of alkali or sodium carbonate, followed by removal of the solvent and reprecipitation from water (**IIa**, **IIb**), vacuum sublimation (**IIIa**, **IIIb**), extraction with diethyl ether (**IVa**–**IVf**), or recrystallization from ethanol (**IIc**–**IIf**, **IIIc**–**IIIf**, **IVc**–**IVf**) or acetone (**IIa**, **IIb**, **IVa**, **IVb**). The products were crystalline, amorphous, or viscous oily substances. Compound **IVb** underwent decomposition upon attempted purification by vacuum distillation. Pyrimidine-2-thiols **IVa**–**IVf** were characterized by a specific odor. The structure of compounds **II**–**IV** was confirmed by their elemental analyses and UV, IR, and ^1H and ^{19}F NMR spectra.

The IR spectra of compounds **IIa**–**IIf** largely resemble those of 2-amino-substituted pyrimidines [3, 11], which are characterized by the presence of absorption bands in the region 3330–3480 cm^{-1} due to stretching vibrations of the amino group. Pyrimidin-2-ol derivatives **IIIa**–**IIIf** displayed in the IR spectra absorption bands belonging to stretching vibrations of the hydroxy group at 3300–3500 cm^{-1}, and the band at 1770–1780 cm^{-1} is likely to arise from tautomeric dihydropyrimidin-2-one structure. In the spectra of pyrimidine-2-thiols **IVa**–**IVf** we observed medium-intensity bands at 2500–2600 and 665 cm^{-1}, which were assigned to stretching vibrations of the S–H and C–S bonds. All 6-perfluoroalkylpyrimidines **II**–**IV** were characterized by IR absorption bands due to stretching vibrations of the methyl C–H bonds (2310–3220 cm^{-1}), stretching vibrations of the C=C and C=N bonds in the pyrimidine ring, bending vibrations of the N–H bonds, skeletal vibrations of the pyrimidine ring (1440–1680 cm^{-1}), and stretching vibrations of the C–F and C–O bonds (900–1340 cm^{-1}) [18].

The UV spectra of 6-perfluoroalkyl-2-aminopyrimidines **IIa**–**IIf** in aqueous alcohol at pH 7 contained one (**IIa**, **IIb**, **IId**, **IIe**) or two absorption maxima (**IIc**, **IIf**) arising from the first (**IIa**–**IIf**, λ_{max} 217–228 nm, log ε 3.04–4.15) and second π–π* transitions (**IIc**, **IIf**, λ_{max} 202–205 nm, log ε 3.98–3.05); these bands confirm the presence of multiple bonds in the heteroring [19]. Compounds **IIIa**, **IIIc**, **IIId**, and **IIIf** in aqueous propan-2-ol at pH 7 showed two absorption maxima at λ 202–218 nm (log ε 2.72–3.30) and λ 217–270 nm (log ε 3.00–3.31), while only the first maximum was present in the UV spectra of **IIIb** and **IIIe**. Pyrimidine-2-thiol derivatives **IVe** and **IVf** were characterized by

two absorption maxima at λ 202 (logε 2.74–3.14) and 217 nm (logε 3.01–3.35), compounds **IVa** and **IVc** displayed only one band at λ 235 nm (logε 3.92–4.29), and a shoulder at λ 212 nm was observed in the spectrum of **IVb**.

The NH proton appeared in the ^{1}H NMR spectra of **IIa** and **IIc**–**IIe** as a broadened signal in the region δ 10.25–10.90 ppm, indicating the presence of two tautomers, amino and imino. The broadened signal at δ 8.95–9.20 ppm in the spectra of compounds **IIIc** and **IIId** was assigned to the NH proton of pyrimidin-2-one tautomer. The thione tautomers of **IVa**, **IVc**, and **IVe** gave rise to a broadened NH signal in the region δ 8.45–8.88 ppm. In addition, compounds **IIa**, **IIc**–**IIe**, **IIIc**, **IIId**, **IVa**, **IVc**, and **IVe** characteristically displayed a singlet at δ 6.90–7.47 ppm (**IIa**, **IId**, **IVa**, **IVc**, **IVe**) or a doublet at δ 7.00 (J_{HF} = 50 Hz, **IIe**), 7.47 (J_{HF} = 34.4 Hz, **IIIc**), 7.70 (J_{HF} = 50 Hz), or 7.75 ppm (J_{HF} = 34.4 Hz) from the 5-H proton in the pyrimidine ring. The SH proton resonated in the ^{1}H NMR spectra of **IVa**, **IVc**, and **IVe** at δ 4.75–4.92 ppm. Upfield three-proton signals in the region δ 1.20–3.34 ppm were assigned to protons in the 4-methyl group. Signals from the fluorine nuclei in the undecafluoro-1-(trifluoromethyl)-2-oxapentyl substituent of compounds **IIc** and **IIIc** were located in the region δ_F 34.00–83.19 ppm of the ^{19}F NMR spectrum.

Thus we have shown that cyclocondensations of unsymmetrical fluorinated β-diketones with guanidine carbonate, urea, and thiourea in propan-2-ol in the presence of a catalytic amount of hydrochloric acid lead to the formation of the corresponding 6-perfluoroalkyl-substituted 2-amino-, 2-hydroxy-, and 2-sulfanyl-4-methylpyrimidines.

EXPERIMENTAL

The UV spectra were measured from aqueous and alcoholic solutions with a concentration of 10^{-4} M (in propan-2-ol) on an SF-26 spectrophotometer using 1-cm cells. The IR spectra were recorded on IKS-29 and Shimadzu IR-470 instruments from samples prepared as thin films or KBr pellets. The ^{1}H NMR spectra were obtained on Bruker WM-250 (250 MHz), Tesla-BS 487C (80 MHz), and Bruker WF-200 spectrometers (200 MHz) from solutions in CD_3OD using hexamethyldisiloxane as internal reference. The ^{19}F NMR spectra were measured on a WF-200 instrument at 200 MHz relative to hexafluorobenzene as external reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform–ethanol (1:1, 3:2, or 4:1) as eluent.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecane-2,4-dione (Ia). Tridecafluoroheptanoyl fluoride, 200 g (0.55 mol), was added dropwise to a mixture of 23.5 g (0.56 mol) of sodium fluoride in 210 ml of acetone. The mixture was kept for 10–15 h at 70°C, washed with water to pH 6–7, and extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. The extract was filtered, and the solvent was distilled off. Yield 46.7 g (21%), yellow oily liquid, bp 176–177°C, n_D^{20} = 1.3160. IR spectrum (film), ν, cm^{-1}: 1000–1350 (C–F), 1450, 1600, 1660, 1780 (C=O), 2950 (C–H), 3500 (O–H). Found, %: C 28.53; F 62.91. $C_{10}H_5F_{13}O_2$. Calculated, %: C 29.72; F 61.11.

Compounds **Ib**–**If** were synthesized in a similar way.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecane-2,4-dione (Ib). Yield 15%, bp 139–141°C (25 mm), n_D^{20} = 1.3095. IR spectrum (film), ν, cm^{-1}: 980–1350 (C–F), 1455, 1590, 1650, 1770 (C=O), 2940, 2985 (C–H). Found, %: C 27.73; F 62.91. $C_{12}H_5F_{17}O_2$. Calculated, %: C 28.59; F 65.96.

5,6,6,6-Tetrafluoro-5-(heptafluoropropoxy)-hexane-2,4-dione (Ic). Yield 18%, bp 78–80°C, n_D^{20} = 1.3048. IR spectrum (film), ν, cm^{-1}: 980–1350 (C–F, C–O), 1430, 1650, 1770 (C=O), 2500, 3000 (C–H), 3450 (O–H). Found, %: C 28.33; F 57.91. $C_9H_5F_{11}O_3$. Calculated, %: C 29.21; F 56.46.

5,7,7,8,10,10,11,11,12,12,12-Undecafluoro-5,8-bis-(trifluoromethyl)-6,9-dioxadodecane-2,4-dione (Id). Yield 22%, bp 115–117°C, n_D^{20} = 1.2980. IR spectrum (film), ν, cm^{-1}: 950–1350 (C–F, C–O), 1440, 1590, 1770 (C=O), 2450, 2990 (C–H), 3410 (O–H). Found, %: C 25.83; F 61.44. $C_{12}H_5F_{17}O_4$. Calculated, %: C 26.88; F 0.24.

5,7,7,8,10,10,11,13,13,14,14,15,15,15-Tetradecafluoro-5,8,11-tris(trifluoromethyl)-6,9,12-trioxapentadecane-2,4-dione (Ie). Yield 23%, bp 156–160°C, n_D^{20} = 1.2950. IR spectrum (film), ν, cm^{-1}: 950–1350 (C–F, C–O), 1450, 1620, 1670, 1770 (C=O), 2960 (C–H), 3480 (O–H). Found, %: C 24.63; F 63.47. $C_{15}H_5F_{23}O_5$. Calculated, %: C 25.66; F 62.23.

5,7,7,8,10,10,11,13,13,14,16,16,17,19,19,20,22,22,23,25,25,26,28,28,29,31,31,32,34,34,35,35,36,36,36-Pentatriacontafluoro-5,8,11,14,17,20,23,26,29,32-decakis(trifluoromethyl)-6,9,12,15,18,21,24,27,30,33-

decaoxahexatriacontane-2,4-dione (If). Yield 23%, bp 180°C (0.1 mm), n_D^{20} = 1.3070. IR spectrum (film), ν, cm^{-1}: 950–1350 (C–F, C–O), 1430, 1720, 1770 (C=O), 2300, 2910 (C–H), 3300 (O–H).

4-Methyl-6-perfluorohexylpyrimidin-2-amine (IIa). Guanidine carbonate salt, 7.04 g (0.04 mol), was dispersed in propan-2-ol, 1 ml of concentrated hydrochloric acid and 32.3 g (0.08 mol) of diketone **Ia** were added, and the mixture was heated for 3 h at 70°C. The mixture was then neutralized with a 5% solution of sodium carbonate, the organic layer was separated and dried over Na_2SO_4, the solvent was distilled off, and the residue was dissolved in acetone and reprecipitated with water. The precipitate was filtered off and dried over phosphoric anhydride. Yield 17.0 g (50%), colorless crystals, mp 126–128°C (from acetone), R_f 0.87 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 228 nm (logε 3.85). IR spectrum (KBr), ν, cm^{-1}: 1145–1350 (C–F); 1580, 1610, 1680, 1740 (C=C, C=N, C=O, δNH); 2960, 3280 (C–H); 3390, 3480 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.90 t (3H, CH_3), 7.25 s (1H, 5-H), 8.18 br.s (1H, NH). Found, %: F 57.80; N 9.89. $C_{11}H_6F_{19}N_3$. Calculated, %: F 57.82; N 9.84.

Compounds **IIb**–**IIf** were synthesized in a similar way.

4-Methyl-6-perfluorooctylpyrimidin-2-amine (IIb). Yield 75%, oily substance, R_f 0.86 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 218 nm (logε 3.04). IR spectrum (film), ν, cm^{-1}: 1110–1360 (C–F); 1440, 1515, 1620, 1665 (C=C, C=N, C=O, δNH); 2910, 3150 (C–H); 3330, 3480 (N–H). Found, %: F 61.35; N 7.91. $C_{13}H_6F_{19}N_3$. Calculated, %: F 61.26; N 7.97.

4-Methyl-6-[1,2,2,2-tetrafluoro-1-(heptafluoropropoxy)ethyl]pyrimidin-2-amine (IIc). Yield 90%, colorless crystals, mp 104–106°C (from EtOH), R_f 0.91 ($CHCl_3$–EtOH, 1:1). UV spectrum, λ_{max}, nm (logε): 205 (3.98), 225 (4.15). IR spectrum (KBr), ν, cm^{-1}: 1280–1300 (C–F, C–O); 1440, 1540, 1620, 1680 (C=C, C=N, C=O, δNH); 3180, 3200 (C–H); 3400 (N–H). ^{1}H NMR spectrum, δ, ppm: 2.02 t (3H, CH_3), 7.47 s (1H, 5-H), 10.35 br.s (1H, NH). Found, %: F 53.27; N 10.67. $C_{10}H_6F_{11}N_3O$. Calculated, %: F 53.15; N 10.60.

4-Methyl-6-[perfluoro(1,4-dimethyl-2,5-dioxaoctyl)]pyrimidin-2-amine (IId). Yield 77%, amorphous substance, R_f 0.88 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 223 nm (logε 3.71). IR spectrum (KBr), ν, cm^{-1}: 1000–1320 (C–F, C–O); 1540, 1640, 1680, 1770 (C=C, C=N, C=O, δNH); 2900, 3220 (C–H); 3380, 3480 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.90 t (3H, CH_3), 7.60 d.d (1H, 5-H, J_{HF} = 6 Hz), 10.75 br.s (1H, NH). Found, %: F 57.79; N 7.47. $C_{13}H_6F_{17}N_3O_2$. Calculated, %: F 57.76; N 7.52.

4-Methyl-6-[perfluoro(1,4,7-trimethyl-2,5,8-trioxaundecyl)]pyrimidin-2-amine (IIe). Yield 80%, amorphous substance, R_f 0.80 ($CHCl_3$–EtOH, 1:1). UV spectum: λ_{max} 217 nm (logε 3.05). IR spectrum (KBr), ν, cm^{-1}: 990–1300 (C–F, C–O); 1635, 1665, 1755 (C=C, C=N, C=O, δNH); 3165 (C–H); 3360, 3480 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.90 t (3H, CH_3), 7.05 s (1H, 5-H), 8.40 s (1H, NH). Found, %: F 60.38; N 5.79. $C_{16}H_6F_{23}N_3O_3$. Calculated, %: F 60.25; N 5.80.

4-Methyl-6-[perfluoro(1,4,7,10,13,16,19,22,25,28-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxadotriacontyl)]pyrimidin-2-amine (IIf). Yield 80%, oily substance, R_f 0.95 ($CHCl_3$–EtOH, 1:1). UV spectrum, λ_{max}, nm (logε): 202 (3.05), 217 (3.27). IR spectrum (film), ν, cm^{-1}: 980–1320 (C–F, C–O); 1440, 1560, 1620, 1680 (C=C, C=N, C=O, δNH); 2990, 3030 (C–H); 3330 (N–H).

4-Methyl-6-perfluorohexylpyrimidin-2-ol (IIIa). Compound **Ia**, 15.0 g (0.04 mol), was added to a mixture of 2.23 g (0.04 mol) of urea and 1 ml of concentrated hydrochloric acid in propan-2-ol, and the mixture was heated for 3–5 h at 80°C. It was then neutralized with a 5% solution of sodium carbonate, the organic layer was separated and dried over sodium sulfate, the solvent was distilled off, and the residue was subjected to vacuum sublimation. Yield 10.0 g (68%), colorless crystals, mp 98–100°C (from acetone), R_f 0.94 ($CHCl_3$–EtOH, 3:2). UV spectrum: λ_{max}, nm (logε): 203 (2.77), 217 (3.00). IR spectrum (KBr), ν, cm^{-1}: 950–1320 (C–F); 1540, 1640, 1720, 1780 (C=C, C=N, C=O, δNH); 2350, 2900, 3200 (C–H); 3400 (OH). ^{1}H NMR spectrum, δ, ppm: 2.02 t (3H, CH_3), 7.47 s (1H, 5-H), 10.35 br.s (1H, NH). Found, %: F 57.70. $C_{11}H_5F_{13}N_2O$. Calculated, %: F 57.69.

Compounds **IIIb**–**IIIf** were synthesized in a similar way.

4-Methyl-6-perfluorooctylpyrimidin-2-ol (IIIb). Yield 60%, colorless crystals, mp 98–100°C (from acetone), R_f 0.93 ($CHCl_3$–EtOH, 4:1). UV spectrum: λ_{max} 210 nm (logε 3.85). IR spectrum (KBr), ν, cm^{-1}: 920–1370 (C–F); 1590, 1660, 1700, 1780 (C=C, C=N, C=O, δNH); 3190, 3220 (C–H); 3350, 3500 (O–H). Found, %: F 61.24. $C_{13}H_5F_{17}N_2O$. Calculated, %: F 61.15.

4-Methyl-6-[1,2,2,2-tetrafluoro-1-(heptafluoropropoxy)ethyl]pyrimidin-2-ol (IIIc). Yield 60%, colorless crystals, mp 178–180°C (from acetone), R_f 0.93 ($CHCl_3$–EtOH, 4:1). UV spectrum, λ_{max}, nm (log ε): 218 (3.30), 270 (3.18). IR spectrum, ν, cm^{-1}: 1100–1380 (C–F, C–O); 1540, 1620, 1660, 1700 (C=C, C=N, C=O, δNH); 2650, 2850, 3200 (C–H), 3450 (O–H). ^1H NMR spectrum, δ, ppm: 1.55 t (3H, CH_3), 7.47 d.d (1H, 5-H, J_{HF} = 10 Hz), 8.95 br.s (1H, NH). Found, %: F 53.07. $C_{10}H_5F_{11}N_2O_2$. Calculated, %: F 53.02.

4-Methyl-6-[perfluoro(1,4-dimethyl-2,5-dioxaoctyl)]pyrimidin-2-ol (IIId). Yield 72%, amorphous substance, R_f 0.92 ($CHCl_3$–EtOH, 3:2). UV spectrum, λ_{max}, nm (log ε): 202 (2.72), 217 (3.02). IR spectrum (KBr), ν, cm^{-1}: 950–1350 (C–F, C–O); 1520, 1580, 1680, 1770 (C=C, C=N, C=O, δNH); 2520, 2850, 3200 (C–H); 3400 (OH). ^1H NMR spectrum, δ, ppm: 1.25 t (3H, CH_3), 7.25 d.d (1H, 5-H, J_{HF} = 11 Hz), 9.20 br.s (1H, NH). Found, %: F 57.71. $C_{13}H_5F_{17}N_2O_3$. Calculated, %: F 57.66.

4-Methyl-6-[perfluoro(1,4,7-trimethyl-2,5,8-trioxaundecyl)]pyrimidin-2-ol (IIIf). Yield 97%, oily substance, R_f 0.91 ($CHCl_3$–EtOH, 4:1). UV spectrum: λ_{max} 210 nm (log ε 3.95). IR spectrum (film), ν, cm^{-1}: 950–1340 (C–F, C–O); 1450, 1560, 1680, 1780 (C=C, C=N, C=O, δNH); 2500, 2880, 3150 (C–H); 3340 (O–H). Found, %: F 60.28. $C_{16}H_5F_{23}N_2O_4$. Calculated, %: F 60.17.

4-Methyl-6-[perfluoro(1,4,7,10,13,16,19,22,25,28-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxadotriacontyl)]pyrimidin-2-ol (IIIf). Yield 95%, oily substance, R_f 0.81 ($CHCl_3$–EtOH, 4:1). UV spectrum, λ_{max}, nm (log ε): 202 (3.13), 217 (3.31). IR spectrum (film), ν, cm^{-1}: 930–1370 (C–F, C–O); 1440, 1690, 1770 (C=C, C=N, C=O, δNH); 2310, 2910, 2970 (C–H); 3300 (O–H).

4-Methyl-6-perfluorohexylpyrimidine-2-thiol (IVa). Compound **Ia**, 28.28 g (0.07 mol), was added to a solution of 6.08 g (0.08 mol) of thiourea and 2 ml of concentrated hydrochloric acid in propan-2-ol, and the mixture was heated for 3–5 h at 70°C. The mixture was then neutralized with a 5% solution of sodium carbonate, the organic phase was separated and dried over sodium sulfate, the solvent was distilled off, and the residue was recrystallized from acetone. Yield 33.0 g (60%), light red crystals, mp 114–116°C (from acetone), R_f 0.59 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 235 nm (log ε 3.92). IR spectrum (KBr), ν, cm^{-1}: 665, 790 (C=S); 1020–1320 (C–F); 1540, 1600, 1680, 1690 (C=C, C=N, δNH); 2350, 2500 (S–H); 2900, 3100, 3250, 3380 (C–H). ^1H NMR spectrum, δ, ppm: 2.80 t (3H, CH_3), 7.05 br.s (1H, 5-H), 8.45 br.s (1H, NH). Found, %: F 55.62; S 7.20. $C_{11}H_5F_{13}N_2S$. Calculated, %: F 55.60; S 7.12.

Compounds **IVb–IVf** were synthesized in a similar way.

4-Methyl-6-perfluorooctylpyrimidine-2-thiol (IVb). Yield 51%, amorphous substance, R_f 0.67 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 212 nm, sh. IR spectrum (KBr), ν, cm^{-1}: 635, 805 (C=S); 970–1390 (C–F); 1430, 1450, 1590, 1770 (C=C, C=N, δNH); 2310 (S–H); 2760, 2980 (C–H). Found, %: F 59.35; S 5.88. $C_{13}H_5F_{17}N_2S$. Calculated, %: F 59.34; S 5.89.

4-Methyl-6-[1,2,2,2-tetrafluoro-1-(heptafluoropropoxy)ethyl]pyrimidine-2-thiol (IVc). Yield 39%, colorless crystals, mp 94–96°C (from EtOH), R_f 0.67 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 235 nm (log ε 4.29). IR spectrum (KBr), ν, cm^{-1}: 666, 769 (C=S); 990–1380 (C–F, C–O); 1540, 1610, 1640, 1660, 1770 (C=C, C=N, δNH); 2400 (S–H); 3130, 3200, 3350 (C–H). ^1H NMR spectrum, δ, ppm: 2.68 t (3H, CH_3), 7.15 br.s (1H, 5-H), 8.88 br.s (1H, NH). Found, %: F 50.98; S 7.84. $C_{10}H_5F_{11}N_2SO$. Calculated, %: F 50.94; S 7.82.

4-Methyl-6-[perfluoro(1,4-dimethyl-2,5-dioxaoctyl)]pyrimidine-2-thiol (IVd). Yield 45%, amorphous substance, R_f 0.92 ($CHCl_3$–EtOH, 1:1). UV spectrum: λ_{max} 206 nm (log ε 3.80). IR spectrum (KBr), ν, cm^{-1}: 709, 744 (C=S); 1107–1330 (C–F, C–O); 1526, 1558, 1640, 1668, 1777 (C=C, C=N, δNH); 2490 (S–H); 2993, 3170, 3340 (C–H). Found, %: F 56.12; S 5.59. $C_{13}H_5F_{17}N_2SO_2$. Calculated, %: F 56.05; S 5.57.

4-Methyl-6-[perfluoro(1,4,7-trimethyl-2,5,8-trioxaundecyl)]pyrimidine-2-thiol (IVe). Yield 57%, oily substance, R_f 0.79 ($CHCl_3$–EtOH, 1:1). UV spectrum, λ_{max}, nm (log ε): 202 (2.74), 217 (3.01). IR spectrum (film), ν, cm^{-1}: 610, 715 (C=S); 995–1330 (C–F, C–O); 1540, 1660, 1770 (C=C, C=N, δNH); 2500 (S–H); 3200, 3300 (C–H). ^1H NMR spectrum, δ, ppm: 2.25 t (3H, CH_3), 7.10 br.s (1H, 5-H), 8,80 br.s (1H, NH). Found, %: F 58.92; S 4.34. $C_{16}H_5F_{23}N_2SO_3$. Calculated, %: F 58.87; S 4.32.

4-Methyl-6-[perfluoro(1,4,7,10,13,16,19,22,25,29-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxadotriacontyl)]pyrimidine-2-thiol (IVf). Yield 70%, oily

substance, R_f 0.91 ($CHCl_3$–EtOH, 1:1). UV spectrum, λ_{max}, nm (log ε): 202 (3.14), 217 (3.35). IR spectrum (film), ν, cm^{-1}: 770, 810 (C=S); 950–1390 (C–F, C–O); 1450, 1550, 1718, 1776 (C=C, C=N, δNH); 2352 (S–H); 2528, 2944, 2992, 3308 (C–H).

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