✾ Synthesis and reactivity of 2-polyfluoroalkylchromene-4(4*H*)-thiones

B. I. Usachev, M. A. Shafeev, and V. Ya. Sosnovskikh★

A. M. Gorky Ural State University,
51 prosp. Lenina, 620083 Ekaterinburg, Russian Federation.
Fax: +7 (343 2) 61 5978. E-mail: Vyacheslav.Sosnovskikh@usu.ru

2-Polyfluoroalkylchromene-4(4*H*)-thiones, synthesized from 2-polyfluoroalkylchromones and P_2S_5, react with aniline, phenylhydrazines, and hydroxylamine at the C(4) atom and afford corresponding anils, phenylhydrazones, and oximes of chromones. On heating in alcohol in the presence of concentrated HCl, chromone phenylhydrazones and oximes undergo ring closure to form 3-(2-hydroxyaryl)-1-phenyl-5-polyfluoroalkylpyrazoles and 5-hydroxy-3-(2-hydroxyaryl)-5-polyfluoroalkyl-Δ^2-isoxazolines.

Key words: 2-polyfluoroalkylchromene-4(4*H*)-thiones, amines, hydrazines, hydroxylamine; anils, chromone phenylhydrazones, chromone oximes; pyrazoles, isoxazolines.

In continuation of our studies of the chemical properties of 2-polyfluoroalkylchromones **1**, which turned out to be highly reactive substrates in reactions with N-, S-, and C-nucleophiles,[1] it seemed of interest to synthesize 2-polyfluoroalkylchromene-4(4*H*)-thiones (**2**) and compare their reactivity toward N-nucleophiles with the reactivity of previously studied 2-polyfluoroalkylchromones **1**. It is known[1—4] that the reactions of chromones with nucleophilic reagents occur mainly at the C(2) atom (1,4 addition), regardless of the presence and nature of a substituent at this atom. The replacement of the carbonyl oxygen atom by the sulfur atom makes it possible, in some cases, to direct the attack of an N-nucleophile to the C(4) atom. For instance, it has been shown[5—7] that 2-arylchromene-4(4*H*)-thiones react with primary amines, hydroxylamine, and hydrazines at the thione group to form the corresponding *N*-substituted flavone imines. Taking into account these data, it could be assumed that 2-R^F-chromenethiones **2**, as 2-R^F-chromones **1**, are valuable substrates for syntheses of a wide series of R^F-containing, including trifluoromethylated, nitrogen heterocycles, which are of interest from the viewpoint of their potential biological activity.[8]

In this work, we synthesized for the first time a series 2-polyfluoroalkylchromene-4(4*H*)-thiones **2** by the reaction of 2-R^F-chromones **1** with P_2S_5 and studied their reactions with different N-nucleophiles. As should be expected in accord with the principle of "hard and soft acids and bases" and published data on 2-arylchromene-4-thiones,[5—7] 2-R^F-chromenethiones **2** react with aniline, phenylhydrazine, and hydroxylamine at the C(4) atom (1,2 addition). This enhances substantially the synthetic significance of the chromone system with a polyfluoroalkyl group in position 2 due to a possibility of obtaining related regioisomeric R^F-containing heterocyclic compounds.

Results and Discussion

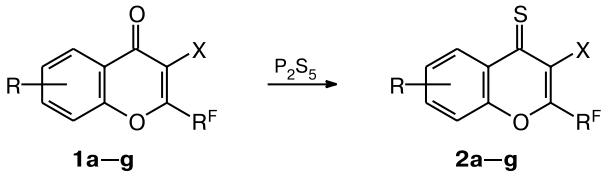
Data on the synthesis and chemical properties of chromenethiones containing a polyhaloalkyl group at the C(2) atom are lacking. At the same time, the reaction of 2-arylchromene-4-thione, chromene-4-thione, 2-methylchromene-4-thione, and their substituted derivatives with different N-nucleophiles were studied in detail. For example, the reagents with the primary amino group were shown to react with 2-arylchromene-4-thiones predominantly at the C(4) atom with the formation of flavone imines, hydrazones, and oximes.[5—7,9] Hydrazine, phenylhydrazine, and hydroxylamine react with chromene-4-thiones both at the C(2) atom with pyrone ring opening and formation of the corresponding pyrazoles and isoxazoles[7,10] and at the C(4) atom.[7,10,11]

We found that reflux of 2-R^F-chromones **1a—g** with P_2S_5 in toluene for 4 h affords 2-R^F-chromenethiones **2a—g** in 49—93% yield. Compounds **2a—g** (Scheme 1) are crystals colored from green to violet. The presence of a halogen atom in position 3 does not prevent the reaction. The replacement of the carbonyl O atom by an S atom results in a substantial downfield shift of signals from the H(3) and H(5) protons (by ~0.7 and ~0.3 ppm, respectively), which is related to a high deshielding effect of the S atom. At the same time, the transition from chromone **1a** to chromenethione **2a** only insignificantly affects the chemical shift of the CF_3 group (−72.2 ppm in **1a** and −71.5 ppm in **2a**).

On refluxing in butanol for 4 h, chromenethiones **2a,b,f** react with aniline at the C(4) atoms to afford anils **3a,b,f**

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2188—2195, October, 2004.

Scheme 1

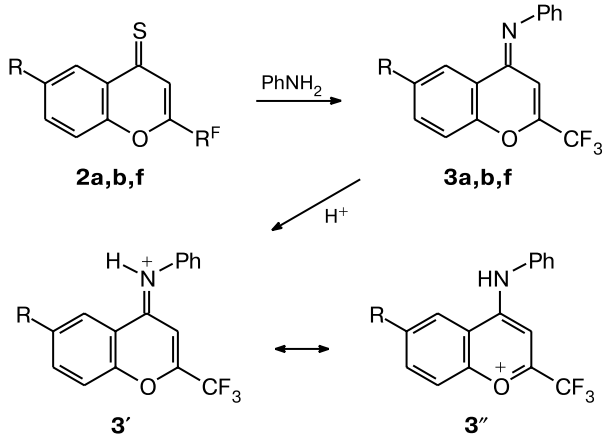


1a—g **2a—g**

	a	**b**	**c**	**d**	**e**	**f**	**g**
R^F	CF_3	CF_3	CF_3	CF_3	CF_3	$(CF_2)_2H$	$(CF_2)_2H$
R	H	6-Me	7-MeO	H	H	H	6-Me
X	H	H	H	Cl	Br	H	H

in 55—79% yields (Scheme 2). When compounds **3** are refluxed in ethanol in the presence of concentrated HCl, they hydrolyze to chromones **1**, whereas in aqueous AcOH the reaction ceases at intermediate 2-hydroxy-2-trifluoromethylchroman-4-ones, as in the case of *N*-alkyl-4*H*-chromene-4-imines recently described by us.[12] It should be mentioned that chromones[10] and even 2-R^F-chromones do not react with aromatic amines (except for 6-nitro-2-trifluoromethylchromone[13] and 5,7-dimethyl-2-trifluoromethyl-8-azachromone,[14] which can undergo pyrone ring opening under the action of aniline to form β-anilinovinyl ketones). 2-Phenylchromene-4-thione does not either react with aniline, and flavone anil was obtained only from more reactive 4-methylthioflavilium, which is formed by the methylation of thione at the sulfur atom under the action of MeI.[6]

Scheme 2



2a,b,f **3a,b,f** **3′** **3″**

The ^{1}H NMR spectra of anils **3** contain only one set of signals corresponding to the *E* configuration of the C=N bond, which can be concluded from the chemical shift value of the H(5) proton (δ 8.13—8.37). Because of unfavorable steric interactions with the *peri*-H atom in the *Z* isomer, the phenyl substituent should predominantly be located in the nonplanar position toward the chromone system and exerts a shielding effect on the H(5) proton. As a result, the H(5) proton should appear in a stronger field (in the series of 4-azafluorene azomethines, a similar proton is observed at 6.1—6.5 ppm).[15,16]

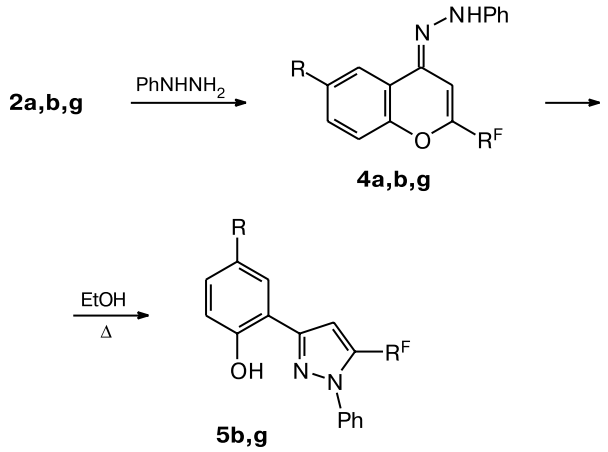
Also note that, unlike *N*-alkylchromeneimines that are protonated in a $CDCl_3$ solution in the presence of both CD_3CO_2D and CF_3CO_2H,[12] compounds **3** form anilium cations **3′** only with CF_3CO_2H. In this case, signals of all protons of the heterocyclic system exhibit a downfield shift by 0.5—0.6 ppm, and the H(3) proton is deshielded to the greatest extent, which is likely related to an increase in the contribution of aromatic chromilium cation **3″**. At the same time, the chemical shifts of protons remain unchanged upon the addition of CD_3CO_2D, indicating a lower basicity of anils **3** and explaining their incapability, unlike *N*-alkylchromeneimines,[12] of opening to form aminoenones in an ammonium acetate solution.

The reactions of aliphatic primary amines (benzylamine, 2-aminoethanol) with chromenethiones **2** occur ambiguously and afford a complicated mixture of substances, whose main components are regioisomeric aminoenones, *viz.*, products of the amino group attack at the C(2) and C(4) atoms of the chromenethione system followed by pyrone ring opening. This fact is in contrast to the behavior of chromones, whose reaction with primary amines at the C(2) atom with the formation of 3-amino-1-(2-hydroxyaryl)prop-2-en-1-ones is one of the most characteristic.[1,2] We failed to isolate individual products in the reactions of substituted anilines, such as *o*-mercaptoaniline.

Compounds **2a,b,g** react with phenylhydrazine already at ~20 °C. The reaction is accompanied by vigorous H_2S evolution and affords (within several min) phenylhydrazones **4a,b,g** (37—78% yields), whose non-fluorinated analogs were synthesized earlier from chromene-4-thiones and 2-arylchromene-4-thiones under more drastic conditions.[7,10,11] On boiling in ethanol in the presence of concentrated HCl, phenylhydrazones **4b,g** undergo ring closure to 1-Ph-5-R^F-pyrazoles **5b,g** in ~100% yield (Scheme 3). The R^F group is located at the C(5) atom (not C(3)), which can easily be established if one considers the $^3J_{H,F}$ constant value of the $(CF_2)_2H$ group in pyrazole **5g**. This constant is 3.2 Hz in a $CDCl_3$ solution and corresponds to the 5-R^F regioisomer[17] ($^3J_{H,F}$ = 4.5 Hz was indicated for the 3-R^F regioisomer).[17] Note that the structure of 5-(2-hydroxyphenyl)-3-methyl-1-phenylpyrazole was ascribed to the product of the reaction of 2-methylchromene-4-thione with phenylhydrazine.[6]

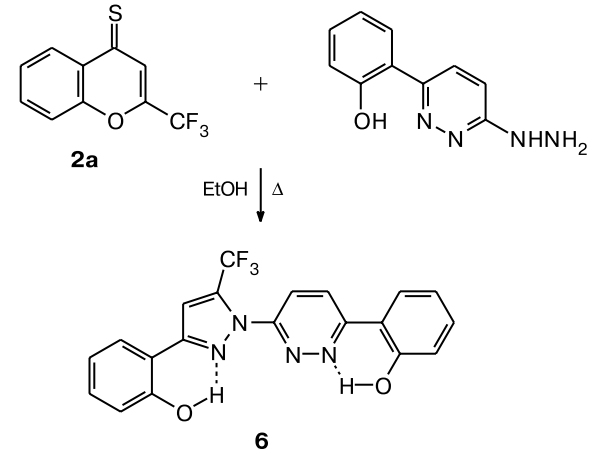
Pyrazoles **5** can be obtained directly from chromenethiones **2** when the latter are refluxed in alcohol with phenylhydrazines. However, from the preparative point of view, this reaction is better to use only in the case of solid hydrazines, where solvent should be used and the process cannot be stopped at the step of phenylhydr-

Scheme 3



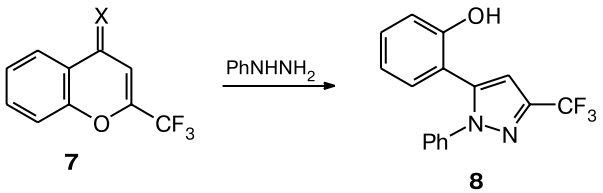
azone **4**. For example, we obtained 3-(5-CF_3-pyrazol-1-yl)pyridazine **6** from chromenethione **2a** and 3-hydrazino-6-(2-hydroxyphenyl)pyridazine[18] on refluxing in methanol (Scheme 4). This compound belongs to the series of 5-R^F-pyrazoles, which is indicated by the chemical shifts of H(6) protons of the 2-hydroxyphenyl substituents (δ 7.93 and 8.20) characteristic of a planar conformer stabilized by two intramolecular hydrogen bonds (IMHB)[19,20] (in the case of 3-R^F regioisomer, no IMHB can be formed between the phenolic proton and pyrazole ring). Chromone **1a** does not react with hydrazinopyridazine.

Scheme 4



We have previously shown[19] that the reaction of 2-R^F-chromones **1** with phenylhydrazine on refluxing in ethanol occurs at the C(2) atom and, unlike chromenethiones **2**, affords 1-Ph-3-R^F-pyrazoles. However, the yields of these compounds did not exceed 20% and, hence, chromones **1** could not be recommended for preparative synthesis of 1-Ph-3-R^F-pyrazoles. Recently described[12,21–23] *N*-alkyl-4*H*-chromene-4-imines turned out to be more appropriate for this purpose. They are protonated at the imine nitrogen atom even in a weakly acidic medium and generate iminium cations with an enhanced electrophilicity of the C(2) atom. We found that *N*-benzyl-2-trifluoromethyl-4*H*-chromene-4-imine (**7**) reacts with $PhNHNH_2$ in a solution of AcOH and EtOH (~20 °C, 10 min) and gives 1-Ph-3-CF_3-pyrazole **8** in 50% yield. Compound **8** was obtained earlier[19] from chromone **1a** in a yield of 13% only (Scheme 5).

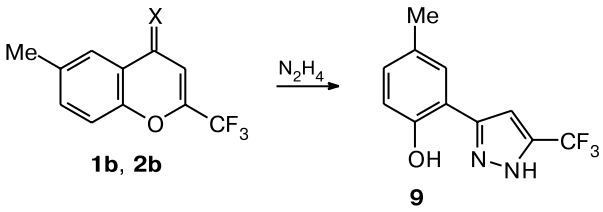
Scheme 5



X = O (**1a**), N-Bn (**7**)

Thus, the replacement of the carbonyl groups in 2-R^F-chromones **1** by the thione or imino group makes it possible to synthesize regioisomeric *N*-substituted pyrazoles. However, anils **3** do not react with phenylhydrazine, under these conditions, because of a lower basicity. The reaction of chromenethione **2b** with hydrazine hydrate occurs as easily as that of chromone **1b**[19] and affords pyrazole **9** in 65% yield (Scheme 6). In this case, unlike the reaction of phenylhydrazine, we failed to detect the formation of chromone hydrazone as an intermediate product. Non-fluorinated chromenethiones react with hydrazine hydrate to afford both pyrazoles[7,10] and hydrazones.[7,11]

Scheme 6



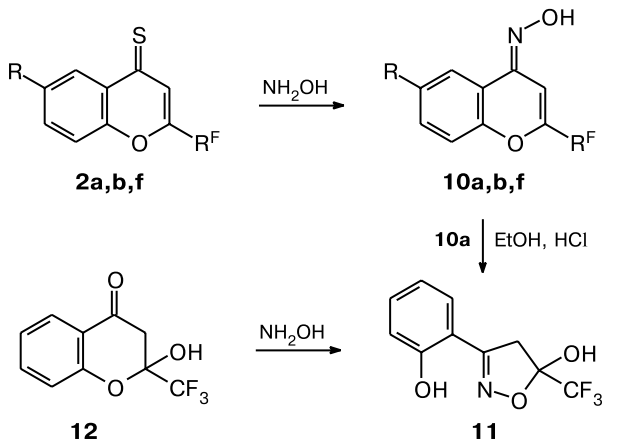
X = O (**1b**), S (**2b**)

The reactions of chromones with hydroxylamine are known to give mainly mixtures of regioisomeric isoxazoles,[3,4,24–28] and the formation of chromone oximes along with isoxazoles was observed only for chromones unsubstituted in position 2[4,24,28] and flavone.[27] The direction of the reaction of chromene-4-thiones with NH_2OH depends, to a great extent, on the nature of

substituents in positions 2 and 3. In this case, 2-arylchromene-4-thiones give predominantly flavone oximes,[6,9] whereas chromone dioximes, isoxazoles, thiazoles, and oximes were obtained in the reactions with chromenethiones and 3-arylchromene-4-thiones.[26,29]

We have recently shown[30] that 2-R^F-chromones **1** react with NH_2OH at the C(2) atom to form monooximes of the corresponding β-diketones, which readily undergo ring closure in an acidic medium to form 3-R^F-isoxazoles. In this work, we found that 2-R^F-chromenethiones **2** react very smoothly and selectively with NH_2OH (ethanol, ~20 °C, 5 min) at the thione group to form chromone oximes **10a,b,f** in 72—83% yields. In addition, only compounds **10** were also obtained from chromenethiones **2** under more drastic conditions (reflux in aqueous ethanol for 1 h). Under these conditions, chromones **1** gave diketone monooximes[30] (Scheme 7). According to the ^1H NMR spectra, oximes **10** are formed almost exclusively as *E* isomers, in the spectra of which signals from the H(5) and H(3) protons are observed at δ 7.71—7.94 and 7.15—7.17, respectively. An insignificant content of the *Z* isomers (2—3% for **10a,b** and 6% for **10f**) can be concluded from the downfield signal of the H(5) proton at δ 8.95—8.97 and the singlet of the H(3) proton at δ 6.40—6.45, which agrees with the published data on the chemical shifts of the H(5) atom in isomeric 3-methylchromone oximes (*Z*-oxime: δ 9.13, *E*-oxime: δ 7.95).[29]

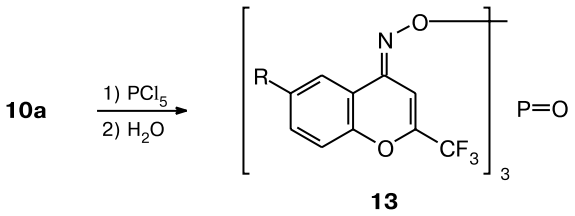
Scheme 7



The simple and efficient synthesis of chromone oximes **10** is of doubtless interest, because this class of organic compounds remained inaccessible and poorly studied up to recently. On refluxing in alcohol in the presence of HCl, oxime **10a** transforms into isoxazoline **11**, which we obtained earlier from 2-hydroxy-2-trifluoromethylchroman-4-one (**12**) and used for the synthesis of the corresponding 5-CF_3-isoxazole[30] (see Scheme 7). Thus, the transition from chromones **1** to chromenethiones **2** changes the direction of the reaction of hydroxylamine with the chromone system, which makes it possible to obtain regioisomeric 5- and 3-polyfluoroalkyl-containing isoxazoles.

It is interesting that, under the conditions of the Beckmann rearrangement, the reaction of oxime **10a** with PCl_5 in ether followed by the hydrolysis of the reaction mixture affords phosphate **13**, whose structure was confirmed by the data of elemental analysis and IR and NMR spectroscopies (Scheme 8).

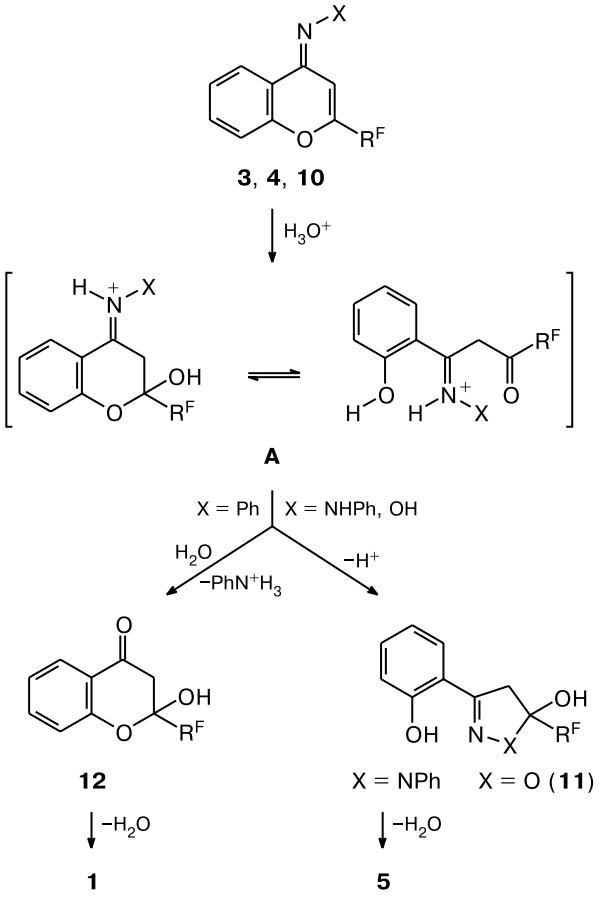
Scheme 8



The formation of different products on refluxing anils **3**, phenylhydrazones **4**, and oximes **10** in alcohol in the presence of concentrated HCl is explained in Scheme 9. The acid-catalyzed hydration of the double bond of the pyrone ring leads to intermediate **A** existing, most likely, as an equilibrium mixture of cyclic and open forms. In the case of anils **3**, this intermediate hydrolyzes to chromanone **12** stable in a weakly acidic medium but easily dehydrating to chromone **1** in the presence of HCl. For X = OH, intermediate **A** undergoes ring closure to form isoxazoline **11** stable under the given conditions,[30] and at X = NHPh intermediate **A** forms pyrazoline that looses a water molecule and transforms into pyrazole **5**. This scheme does not contradict the mechanism of hydrolysis of *N*-alkylchromeneimines to aminoenones and chromanones[12] that has been proposed by us previously.

The different behavior of compounds **1** and **2** in the reactions with N-nucleophiles agrees well with the semiempirical quantum-chemical calculations for chromone **1a** and chromenethione **2a** performed using the PM3 method.[31] The results of calculations show that **1a** and **2a** differ slightly by LUMO energy (−1.15 and −1.26 eV, respectively), whereas the atomic coefficients of the p_z orbitals of the C(2) and C(4) atoms in LUMO are equal to −0.51 and 0.37 (for **1a**) and −0.40 and 0.56 (for **2a**), predicting the predominant attack to the C(2) atom of chromone **1a** and to the C(4) atom of chromenethione **2a** by a nucleophilic species. In addition, the calculations of the reaction routes of addition at the carbonyl and thione groups for the reaction of compounds **1a** and **2a** with hydroxylamine show a much higher activation energy (45 kcal mol^{-1}) for the attack to the C=O bond by hydr-

Scheme 9



oxylamine, while for the C=S bond the activation energy is only 18 kcal mol^{-1}.

It should be noted in conclusion that with 2-CF_3-chromenethione **2a** we could not perform the whole series of reactions that were characteristic of 2-phenylchromene-4-thione and 2-CF_3-chromones **1**. For example, unlike phenylchromenethione, chromenethione **2a**, being treated with MeI, is not methylated at the sulfur atom. Under the conditions where phenylchromenethione hydrolyzes to flavone in 65% yield,[6] chromenethione **2a** gives chromone **1a** only in trace amounts. Chromenethione **2a** does not react either with (trifluoromethyl)trimethylsilane (reacting with 2-CF_3-chromones by the type of 1,4 addition[32,33]), does not react with ethylmercaptoacetate (in the reaction with which 2-CF_3-chromones afford dihydrothienocoumarins[34,35]), and transforms into resin under the action of phenyllithuim at −50 °C.

Thus, unlike earlier studied 2-R^F-chromones,[1] 2-R^F-chromenethiones react with N-nucleophiles mainly according to the 1,2 addition type, which makes it possible to obtain anils, phenylhydrazones, and oximes of 2-R^F-chromones inaccessible by other methods and being of interest for further studies in the field of regiocontrolled synthesis of polyfluoroalkyl-containing heterocyclic compounds.

Experimental

IR spectra were recorded on IKS-29 and Perkin—Elmer Spectrum BX-II instruments in Nujol or KBr pellets. ^{1}H NMR spectra were obtained on a Bruker DRX-400 spectrometer in $CDCl_3$ with a working frequency of 400.1 MHz and Me_4Si as an internal standard. The starting chromones **1a—d,f,g** [30,36,37] and chromeneimine **7** [22] were described earlier.

3-Bromo-2-trifluoromethylchromone (1e) was synthesized by a procedure similar to that described for 3-chloro-2-trifluoromethylchromone[36] in 72% yield, m.p. 149—150 °C (ethanol), colorless needle-like crystals. Found (%): C, 41.32; H, 1.37. $C_{10}H_4BrF_3O_2$. Calculated (%): C, 40.99; H, 1.38. IR, ν/cm^{-1}: 1660 (C=O), 1620 (C=C), 1575 (arom.). ^{1}H NMR ($CDCl_3$), δ: 7.54 (ddd, 1 H, H(6), J_o = 8.1 Hz, 7.2 Hz, J_m = 1.0 Hz); 7.58 (d, 1 H, H(8), J_o = 8.6 Hz); 7.81 (ddd, 1 H, H(7), J_o = 8.6, 7.2 Hz, J_m = 1.7 Hz); 8.27 (dd, 1 H, H(5), J_o = 8.1 Hz, J_m = 1.7 Hz).

Synthesis of 2-polyfluoroalkylchromene-4(4*H*)-thiones (2) (general procedure). A mixture of 2-R^F-chromone **1** (4.5 mmol) and P_2S_5 (1.0 g, 4.5 mmol) in anhydrous toluene (5 mL) was refluxed with stirring for 4 h. After the reaction mixture cooled down, it was filtered, the solvent from the filtrate was evaporated, and the residue was recrystallized from hexane (a hot hexane solution was preliminarily passed through silica gel (2 cm^3)). All synthesized chromenethiones are brightly colored crystalline substances stable on storing for several weeks.

2-Trifluoromethylchromene-4-thione (2a). The yield was 93%, m.p. 71—72 °C, dark blue needle-like crystals with metallic luster. Found (%): C, 52.04; H, 2.20. $C_{10}H_5F_3OS$. Calculated (%): C, 52.17; H, 2.19. IR (KBr), ν/cm^{-1}: 3065, 1640, 1605. ^{1}H NMR ($CDCl_3$), δ: 7.44 (s, 1 H, H(3)); 7.46 (ddd, 1 H, H(6), J_o = 8.2, 7.1 Hz, J_m = 1.1 Hz); 7.53 (dd, 1 H, H(8), J_o = 8.6 Hz, J_m = 1.1 Hz); 7.78 (ddd, 1 H, H(7), J_o = 8.6, 7.1 Hz, J_m = 1.6 Hz); 8.48 (dd, 1 H, H(5), J_o = 8.2 Hz, J_m = 1.6 Hz). ^{19}F NMR (376.5 MHz, $CDCl_3$, $CFCl_3$), δ: −71.5 (CF_3).

6-Methyl-2-trifluoromethylchromene-4-thione (2b). The yield was 60%, m.p. 77—79 °C, light green crystals. Found (%): C, 53.16; H, 2.89. $C_{11}H_7F_3OS \cdot 0.25H_2O$. Calculated (%): C, 53.12; H, 2.84. IR, ν/cm^{-1}: 1635, 1560. ^{1}H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, Me); 7.43 (d, 1 H, H(8), J_o = 8.6 Hz); 7.44 (s, 1 H, H(3)); 7.60 (ddq, 1 H, H(7), J_o = 8.6 Hz, J_m = 2.2 Hz, $^4J_{H,Me}$ = 0.5 Hz); 8.28 (dq, 1 H, H(5), J_m = 2.2 Hz, $^4J_{H,Me}$ = 0.5 Hz).

7-Methoxy-2-trifluoromethylchromene-4-thione (2c). The yield was 75%, m.p. 106—108 °C, lilac crystals. Found (%): C, 50.83; H, 2.82. $C_{11}H_7F_3O_2S$. Calculated (%): C, 50.77; H, 2.71. IR (KBr), ν/cm^{-1}: 1645, 1610, 1500. ^{1}H NMR ($CDCl_3$), δ: 3.94 (s, 3 H, MeO); 6.89 (d, 1 H, H(8), J_m = 2.5 Hz); 7.04 (dd, 1 H, H(6), J_o = 9.1 Hz, J_m = 2.5 Hz); 7.36 (s, 1 H, H(3)); 8.42 (d, 1 H, H(5), J_o = 9.1 Hz).

3-Chloro-2-trifluoromethylchromene-4-thione (2d). The yield was 89%, m.p. 72—74 °C, green crystals. Found (%): C, 45.13; H, 1.54. $C_{10}H_4ClF_3OS$. Calculated (%): C, 45.38; H, 1.52. IR, ν/cm^{-1}: 1605, 1600. ^{1}H NMR (DMSO-d_6), δ: 7.65 (ddd, 1 H, H(6), J_o = 8.2, 7.1 Hz, J_m = 1.1 Hz); 7.84 (ddd, 1 H, H(8), J_o = 8.5 Hz, J_m = 1.1 Hz, J_p = 0.4 Hz); 7.99 (ddd, 1 H, H(7),

J_o = 8.5, 7.1 Hz, J_m = 1.6 Hz); 8.42 (ddd, 1 H, H(5), J_o = 8.2 Hz, J_m = 1.6 Hz, J_p = 0.4 Hz).

3-Bromo-2-trifluoromethylchromene-4-thione (2e). The yield was 49%, m.p. 88—89 °C, green needle-like crystals. Found (%): C, 38.79; H, 1.25. $C_{10}H_4BrF_3OS$. Calculated (%): C, 38.86; H, 1.30. IR, ν/cm^{-1}: 1605, 1590. ^{1}H NMR ($CDCl_3$), δ: 7.54 (ddd, 1 H, H(6), J_o = 8.0, 7.2 Hz, J_m = 1.0 Hz); 7.58 (ddd, 1 H, H(8), J_o = 8.6 Hz, J_m = 1.0 Hz, J_p = 0.5 Hz); 7.81 (ddd, 1 H, H(7), J_o = 8.6, 7.2 Hz, J_m = 1.7 Hz); 8.26 (ddd, 1 H, H(5), J_o = 8.0 Hz, J_m = 1.7 Hz, J_p = 0.5 Hz).

2-(1,1,2,2-Tetrafluoroethyl)chromene-4-thione (2f). The yield was 64%, m.p. 63—65 °C, violet needle-like crystals with metallic luster. Found (%): C, 50.37; H, 2.42. $C_{11}H_6F_4OS$. Calculated (%): C, 50.38; H, 2.31. IR, ν/cm^{-1}: 1635, 1610. ^{1}H NMR ($CDCl_3$), δ: 6.14 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 3.5 Hz); 7.46 (s, 1 H, H(3)); 7.47 (ddd, 1 H, H(6), J_o = 8.2, 7.1 Hz, J_m = 1.1 Hz); 7.51 (ddd, 1 H, H(8), J_o = 8.6 Hz, J_m = 1.1 Hz, J_p = 0.5 Hz); 7.77 (ddd, 1 H, H(7), J_o = 8.6, 7.1 Hz, J_m = 1.7 Hz); 8.50 (ddd, 1 H, H(5), J_o = 8.2 Hz, J_m = 1.7 Hz, J_p = 0.5 Hz).

6-Methyl-2-(1,1,2,2-tetrafluoroethyl)chromene-4-thione (2g). The yield was 92%, m.p. 96—98 °C, violet needle-like crystals with metallic luster. Found (%): C, 52.46; H, 3.03. $C_{12}H_8F_4OS$. Calculated (%): C, 52.17; H, 2.92. IR, ν/cm^{-1}: 1635, 1565. ^{1}H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, Me); 6.13 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.0 Hz, $^3J_{H,F}$ = 3.5 Hz); 7.41 (d, 1 H, H(8), J_o = 8.6 Hz); 7.46 (s, 1 H, H(3)); 7.59 (ddq, 1 H, H(7), J_o = 8.6 Hz, J_m = 2.2 Hz, $^4J_{H,Me}$ = 0.5 Hz); 8.29 (dq, 1 H, H(5), J_m = 2.2 Hz, $^4J_{H,Me}$ = 0.5 Hz).

Synthesis of 2-polyfluoroalkylchromone anils (3) (general procedure). A mixture of the corresponding 2-R^F-chromene-4-thione **2** (6.5 mmol) and freshly distilled aniline (0.75 g, 8.1 mmol) in anhydrous butanol (5 mL) was refluxed for 4 h. Then the reaction mixture was placed in a Petri dish, and after the solvent evaporated, the residue was recrystallized from ethanol or hexane.

***N*-(2-Trifluoromethyl-4*H*-chromen-4-ylidene)aniline (3a).** The yield was 79%, m.p. 103—104 °C, yellow crystals. Found (%): C, 66.07; H, 3.59; N, 4.91. $C_{16}H_{10}F_3NO$. Calculated (%): C, 66.44; H, 3.48; N, 4.84. IR (KBr), ν/cm^{-1}: 1665, 1640, 1615, 1600, 1590, 1580. ^{1}H NMR ($CDCl_3$), δ: 6.57 (s, 1 H, H(3)); 6.87—6.90 (m, 2 H, arom.); 7.14 (tt, 1 H, arom., J_o = 7.4 Hz, J_m = 1.2 Hz); 7.35—7.42 (m, 4 H, H(6), H(8), arom.); 7.60 (ddd, 1 H, H(7), J_o = 8.4, 7.2 Hz, J_m = 1.7 Hz); 8.36 (dd, 1 H, H(5), J_o = 8.0 Hz, J_m = 1.7 Hz). ^{1}H NMR ($CDCl_3$+CF_3CO_2H), δ: 7.16 (s, 1 H, H(3)); 7.42—7.45 (m, 2 H, arom.); 7.57—7.64 (m, 3 H, arom.); 7.83—7.88 (m, 2 H, H(6), H(8)); 8.11 (ddd, 1 H, H(7), J_o = 8.6, 7.3 Hz, J_m = 1.4 Hz); 8.85 (dd, 1 H, H(5), J_o = 8.1 Hz, J_m = 1.4 Hz).

Heating of anil **3a** in aqueous AcOH under the conditions described for hydrolysis of chromeneimines[12] gave chromanone **12** in 72% yield and m.p. 153—154 °C (*cf.* Ref. 12: m.p. 153—154 °C).

***N*-(6-Methyl-2-trifluoromethyl-4*H*-chromen-4-ylidene)aniline (3b).** The yield was 55%, m.p. 119—121 °C, yellow crystals. Found (%): C, 67.40; H, 3.96; N, 4.47. $C_{17}H_{12}F_3NO$. Calculated (%): C, 67.33; H, 3.99; N, 4.62. IR, ν/cm^{-1}: 1660, 1600, 1585. ^{1}H NMR (acetone-d_6), δ: 2.47 (s, 3 H, Me); 6.59 (s, 1 H, H(3)); 6.91—6.94 (m, 2 H, arom.); 7.15 (tt, 1 H, arom., J_o = 7.4 Hz, J_m = 1.1 Hz); 7.40 (d, 1 H, H(8), J_o = 8.6 Hz); 7.39—7.43 (m, 2 H, arom.); 7.56 (ddq, 1 H, H(7), J_o = 8.6 Hz, J_m = 2.2 Hz, $^4J_{H,Me}$ = 0.5 Hz); 8.13 (br.d, 1 H, H(5), $J_m \approx$ 2.0 Hz).

***N*-(1,1,2,2-Tetrafluoroethyl-4*H*-chromen-4-ylidene)aniline (3f).** The yield was 77%, m.p. 94—95 °C, yellow needle-like crystals. Found (%): C, 63.41; H, 3.46; N, 4.36. $C_{17}H_{11}F_4NO$. Calculated (%): C, 63.56; H, 3.45; N, 4.36. IR, ν/cm^{-1}: 1660, 1590, 1580. ^{1}H NMR ($CDCl_3$), δ: 6.07 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.1 Hz, $^3J_{H,F}$ = 4.2 Hz); 6.59 (s, 1 H, H(3)); 6.88—6.91 (m, 2 H, arom.); 7.14 (tt, 1 H, arom., J_o = 7.4 Hz, J_m = 1.2 Hz); 7.32 (dd, 1 H, H(8), J_o = 8.4 Hz, J_m = 0.9 Hz); 7.36—7.42 (m, 3 H, H(6), arom.); 7.58 (ddd, 1 H, H(7), J_o = 8.5 Hz, 7.2 Hz, J_m = 1.7 Hz); 8.37 (dd, 1 H, H(5), J_o = 8.0 Hz, J_m = 1.7 Hz).

Synthesis of chromone *N*-phenylhydrazones (4) (general procedure). A mixture of chromenethione **2** (4.3 mmol) and freshly distilled phenylhydrazine (0.97 g, 9.0 mmol) was stirred without a solvent for 15 min (the reaction was accompanied by vigorous H_2S evolution). Then the reaction mixture was thoroughly triturated with water (10 mL) until a crystalline product formed. The product was filtered off, washed with water, dried, and recrystallized from hexane.

2-Trifluoromethyl-4*H*-chromen-4-one *N*-phenylhydrazone (4a). The yield was 78%, m.p. 128—129 °C, yellow crystals. Found (%): C, 63.14; H, 3.66; N, 9.04. $C_{16}H_{11}F_3N_2O$. Calculated (%): C, 63.16; H, 3.64; N, 9.21. IR (KBr), ν/cm^{-1}: 3320, 1665, 1640, 1605, 1585, 1560, 1505. ^{1}H NMR ($CDCl_3$), δ: 6.62 (s, 1 H, H(3)); 6.91 (tt, 1 H, arom., J_o = 7.3 Hz, J_m = 1.2 Hz); 7.16—7.33 (m, 7 H, H(6), H(8), NH, arom.); 7.37 (ddd, 1 H, H(7), J_o = 8.3, 7.3 Hz, J_m = 1.7 Hz); 8.14 (dd, 1 H, H(5), J_o = 7.9 Hz, J_m = 1.7 Hz).

6-Methyl-2-trifluoromethyl-4*H*-chromen-4-one *N*-phenylhydrazone (4b). The yield was 37%, m.p. 160—161 °C, yellow crystals. Found (%): C, 64.16; H, 3.92; N, 8.80. $C_{17}H_{13}F_3N_2O$. Calculated (%): C, 64.15; H, 4.12; N, 8.80. IR (KBr), ν/cm^{-1}: 3325, 1660, 1600, 1565, 1505. ^{1}H NMR ($CDCl_3$), δ: 2.41 (s, 3 H, Me); 6.62 (s, 1 H, H(3)); 6.91 (t, 1 H, arom., J_o = 7.3 Hz); 7.07 (d, 1 H, H(8), J_o = 8.4 Hz); 7.17 (br.dd, 1 H, H(7), J_o = 8.4 Hz, $J_m \approx$ 1.7 Hz); 7.18—7.21 (m, 2 H, arom.); 7.29—7.33 (m, 3 H, arom., NH); 7.93 (br.d, 1 H, H(5), $J_m \approx$ 1.5 Hz).

6-Methyl-2-(1,1,2,2-tetrafluoroethyl)-4*H*-chromen-4-one *N*-phenylhydrazone (4g). The yield was 54%, m.p. 135—136 °C, yellow crystals. Found (%): C, 61.49; H, 3.78; N, 8.09. $C_{18}H_{14}F_4N_2O$. Calculated (%): C, 61.72; H, 4.03; N, 8.00. IR, ν/cm^{-1}: 1655, 1605, 1560. ^{1}H NMR ($CDCl_3$), δ: 2.40 (s 3 H, Me); 6.11 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.1 Hz, $^3J_{H,F}$ = 4.5 Hz); 6.59 (s, 1 H, H(3)); 6.90 (t, 1 H, arom., J_o = 7.3 Hz); 7.02 (d, 1 H, H(8), J_o = 8.4 Hz); 7.15 (br.dd, 1 H, H(7), J_o = 8.4 Hz, $J_m \approx$ 1.7 Hz); 7.18—7.21 (m, 2 H, arom.); 7.29—7.33 (m, 3 H, arom., NH); 7.93 (br.d, 1 H, H(5), $J_m \approx$ 1.5 Hz).

Ring closure of *N*-*N*-phenylhydrazones 4b,g to 1-Ph-5-R^F-pyrazoles 5b,g (general procedure). Phenylhydrazone **4** (0.9 mmol) was refluxed for 1 h in ethanol (3 mL) acidified with 3 droplets of concentrated HCl. After the solvent evaporated, the residue was diluted with water (5 mL), a precipitate was filtered off, washed with water, dried, and recrystallized from hexane. The yield of pyrazole **5b** described in Ref. 19 was 89%.

Under these conditions, pyrazoles **5b,g** were synthesized from chromenethiones **2b,g** and phenylhydrazine in ~60% yield, and anils **3a,b** hydrolyze to chromones **1a,b** in ~70% yield.

3-(2-Hydroxy-5-methylphenyl)-1-phenyl-5-(1,1,2,2-tetrafluoroethyl)pyrazole (5g). The yield was 85%, m.p. 69—70 °C, colorless needle-like crystals. Found (%): C, 61.45; H, 4.01;

N, 7.98. $C_{18}H_{14}F_4N_2O$. Calculated (%): C, 61.72; H, 4.03; N, 8.00. IR, ν/cm^{-1}: 3150, 1635, 1600, 1565. ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, Me); 5.84 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.4 Hz, $^3J_{H,F}$ = 3.2 Hz); 6.93 (d, 1 H, H(3), J_o = 8.3 Hz); 7.08 (dd, 1 H, H(4), J_o = 8.3 Hz, J_m = 2.0 Hz); 7.14 (s, 1 H, =CH); 7.40 (br.d, 1 H, H(6), $J_m \approx$ 1.7 Hz), 7.51 (s, 5 H, Ph); 10.00 (s, 1 H, OH).

6-(2-Hydroxyphenyl)-3-[2-(hydroxyphenyl)-5-trifluoromethyl-1*H*-pyrazol-3-yl]pyridazine (6). A mixture of chromenethione **2a** (0.18 g, 0.78 mmol) and 3-hydrazino-6-(2-hydroxyphenyl)pyridazine monohydrate[18] (0.12 g, 0.54 mmol) in methanol (2.5 mL) was refluxed for 1 h. A precipitate that formed when the mixture cooled down was filtered off, washed with methanol, and dried. Compound **6** was obtained in 28% yield (0.05 g) as colorless crystals with m.p. 254—255 °C. Found (%): C, 59.46; H, 3.37; N, 13.68. $C_{20}H_{13}F_3N_4O_2 \cdot 0.25H_2O$. Calculated (%): C, 59.63; H, 3.38; N, 13.91. IR, ν/cm^{-1}: 3265, 1660, 1615, 1595, 1565, 1520, 1495. ^{1}H NMR (DMSO-d_6), δ: 6.94—6.98 (m, 2 H, H(3), H(5)); 7.31 (ddd, 1 H, H(4), J_o = 8.2, 7.4 Hz, J_m = 1.5 Hz); 7.37—7.42 (m, 2 H, H(3′), H(5′)); 7.53 (ddd, 1 H, H(4′), J_o = 8.2, 7.4 Hz, J_m = 1.6 Hz); 7.82 (s, 1 H, pyraz.); 7.93 (d, 1 H, H(6), J_o = 7.9 Hz); 7.93 (d, 1 H, pyrid., J = 9.6 Hz); 8.20 (dd, 1 H, H(6′), J_o = 7.9 Hz, J_m = 1.5 Hz); 8.36 (d, 1 H, pyrid., J = 9.6 Hz); 11.47, 13.16 (both s, 1 H each, OH).

Reaction of *N*-benzyl-2-trifluoromethyl-4*H*-chromene-4-imine (7) with phenylhydrazine. Chromeneimine **7**[22] (0.20 g, 0.66 mmol) was added to a solution of phenylhydrazine (0.09 g, 0.83 mmol) in an AcOH—EtOH (1 : 1) mixture (2 mL), and the resulting reaction mixture was stirred at ~20 °C for 10 min. Then concentrated HCl (0.5 mL) and water (10 mL) were added to the mixture, and an oil that precipitated was triturated to crystallization. The product was filtered off, washed with water, dried, and recrystallized from hexane. 5-(2-Hydroxyphenyl)-1-phenyl-3-trifluoromethylpyrazole (**8**) was obtained in 50% yield (0.10 g) as colorless crystals with m.p. 143—144 °C. Pyrazole **8** was synthesized previously[19] from chromone **1a** in 13% yield with m.p. 144—145 °C.

Reaction of 6-methyl-2-trifluoromethylchromene-4-thione (2b) with hydrazine hydrate. A mixture of chromenethione **2b** (0.20 g, 0.82 mmol) and hydrazine hydrate (0.20 g, 4.0 mmol) in ethanol (1 mL) was stirred at ~20 °C for 1 h. Then the reaction mixture was diluted with water (5 mL), and the precipitate was filtered off, washed with water, dried, and recrystallized from toluene. 3(5)-(2-Hydroxy-5-methylphenyl)-5(3)-trifluoromethylpyrazole (**9**) was obtained in 65% yield (0.13 g) as colorless crystals with m.p. 211—212 °C. Pyrazole **9** was synthesized previously[19] from chromone **1b** in 66% yield with m.p. 210—211 °C.

Synthesis of 2-polyfluoroalkylchromone oximes (10) (general procedure). Hydroxylamine hydrochloride (7.5 mmol), KOH (7.0 mmol), and chromenethione **2** (2.0 mmol) were added successively to ethanol (5 mL), and the resulting mixture were stirred at ~20 °C for 5 min (the reaction was accompanied by vigorous H_2S evolution). Then the reaction mixture was diluted with water (10 mL), and the precipitate was filtered off, washed with water, dried, and recrystallized from heptane.

In addition, oximes **10** are formed in ~75% yield in the reaction of chromenethiones **2** with $NH_2OH \cdot HCl$ in the presence of AcONa according to a procedure described earlier for the synthesis of β-diketone monooximes from chromones **1**[30].

2-Trifluoromethyl-4*H*-chromen-4-one oxime (10a). The yield was 72%, m.p. 155—156 °C, colorless needle-like crystals. Found (%): C, 52.17; H, 2.65; N, 5.92. $C_{10}H_6F_3NO_2$. Calculated (%): C, 52.41; H, 2.64; N, 6.11. IR, ν/cm^{-1}: 3150, 1670, 1620, 1605. ^{1}H NMR ($CDCl_3$), δ: 7.17 (s, 1 H, H(3)); 7.25—7.30 (m, 2 H, H(6), H(8)); 7.47 (ddd, 1 H, H(7), J_o = 8.3, 7.3 Hz, J_m = 1.7 Hz); 7.92 (ddd, 1 H, H(5), J_o = 7.8 Hz, J_m = 1.7 Hz, J_p = 0.6 Hz); 8.21 (s, 1 H, OH).

Reflux of oxime **10a** (0.20 g, 0.87 mmol) in a mixture of ethanol (4 mL) and concentrated HCl (1 mL) for 1 h gave 5-hydroxy-3-(2-hydroxyphenyl)-5-trifluoromethyl-Δ^2-isoxazoline (**11**) in 70% yield (0.15 g) with m.p. 123—124 °C (*cf.* Ref. 30: m.p. 122—123 °C).

6-Methyl-2-trifluoromethyl-4*H*-chromen-4-one oxime (10b). The yield was 75%, m.p. 191—193 °C, colorless needle-like crystals. Found (%): C, 54.40; H, 3.35; N, 5.77. $C_{11}H_8F_3NO_2$. Calculated (%): C, 54.33; H, 3.32; N, 5.76. IR (KBr), ν/cm^{-1}: 3275, 1675, 1630, 1615, 1495. ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 3 H, Me); 7.15 (s, 1 H, H(3)); 7.16 (d, 1 H, H(8), J_o = 8.5 Hz); 7.27 (ddq, 1 H, H(7), J_o = 8.5 Hz, J_m = 2.1 Hz, $^4J_{H,Me}$ = 0.4 Hz); 7.71 (br.d, 1 H, H(5), $J_m \approx$ 1.8 Hz); 7.73 (s, 1 H, OH).

2-(1,1,2,2-Tetrafluoroethyl)-4*H*-chromen-4-one oxime (10f). The yield was 83%, m.p. 148—149 °C, colorless needle-like crystals. Found (%): C, 50.50; H, 2.85; N, 5.24. $C_{11}H_7F_4NO_2$. Calculated (%): C, 50.59; H, 2.70; N, 5.36. IR (KBr), ν/cm^{-1}: 3200, 1665, 1615, 1595, 1570. ^{1}H NMR ($CDCl_3$), δ: 6.09 (tt, 1 H, CF_2CF_2H, $^2J_{H,F}$ = 53.1 Hz, $^3J_{H,F}$ = 4.2 Hz); 7.16 (s, 1 H, H(3)); 7.22 (ddd, 1 H, H(8), J_o = 8.4 Hz, J_m = 1.2 Hz, J_p = 0.4 Hz); 7.27 (ddd, 1 H, H(6), J_o = 8.0 Hz, 7.3, J_m = 1.2 Hz); 7.46 (ddd, 1 H, H(7), J_o = 8.4 Hz, 7.3 Hz, J_m = 1.7 Hz); 7.60 (s, 1 H, OH); 7.94 (ddd, 1 H, H(5), J_o = 8.0 Hz, J_m = 1.7 Hz, J_p = 0.4 Hz).

Oxo(tris{[(2-trifluoromethyl-4*H*-chromen-4-ylidene)amino)]oxy})phosphorane (13). Phosphorus pentachloride (0.54 g, 2.6 mmol) was added to a solution of oxime **10** (0.30 g, 1.3 mmol) in Et_2O (10 mL), and the resulting mixture was stirred for 0.5 h at ~20 °C. A plentiful white precipitate (presumably, the product of substitution of three chlorine atoms in PCl_5 by oxime residues) formed. Then water (5 mL) was added dropwise to the reaction mixture (the precipitate dissolved), and the resulting mixture was diluted with water (25 mL). The solution was extracted with ether (15 mL), the ethereal layer was separated and evaporated, and the residue was recrystallized from a toluene—hexane (1 : 2) mixture. The yield was 0.17 g (54%), colorless powder without distinct melting temperature (melts in an interval of 160—170 °C). Found (%): C, 48.75; H, 2.09; N, 5.85. $C_{30}H_{15}F_9N_3O_7P$. Calculated (%): C, 49.26; H, 2.07; N, 5.75. The substance contains 0.7% Cl, which corresponds to 8.0% admixture of a nonhydrolyzed dichlorosubstituted derivative. IR (KBr), ν/cm^{-1}: 1665, 1615, 1595, 1570. ^{1}H NMR (DMSO-d_6), δ: 7.28 (s, 1 H, H(3)); 7.45 (ddd, 1 H, H(6), J_o = 8.1, 7.3 Hz, J_m = 1.0 Hz); 7.59 (dd, 1 H, H(8), J_o = 8.5 Hz, J_m = 1.0 Hz); 7.76 (ddd, 1 H, H(7), J_o = 8.5, 7.3 Hz, J_m = 1.6 Hz); 7.96 (dd, 1 H, H(5), J_o = 8.1 Hz, J_m = 1.6 Hz). The singlet at 7.28 ppm does not disappear upon CD_3CO_2D addition.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-32706), the Civil Research and Development Foundation (CRDF) of the USA, and the Ministry of Education and

Science of the Russian Federation (Grants EK-005-X1 and Y1-005-04).

References

1. V. Ya. Sosnovskikh, *Usp. Khim.*, 2003, **72**, 550 [*Russ. Chem. Rev.*, 2003, **72**, 489 (Engl. Transl.)].
2. G. P. Ellis, *Chromenes, Chromanones, and Chromones*, in *The Chemistry of Heterocyclic Compounds*, Ed. G. P. Ellis, Wiley, New York, 1977, **31**.
3. C. Morin and R. Beugelmans, *Tetrahedron*, 1977, **33**, 3183.
4. V. Szaby, J. Borbély, E. Theisz, and S. Nagy, *Tetrahedron*, 1986, **42**, 4215.
5. W. Baker, J. B. Harborne, and W. D. Ollis, *J. Chem. Soc.*, 1952, 1294.
6. W. Baker, J. B. Harborne, and W. D. Ollis, *J. Chem. Soc.*, 1952, 1303.
7. W. Baker, G. G. Clarke, and J. B. Harborne, *J. Chem. Soc.*, 1954, 998.
8. T. Hiyama, *Organofluorine Compounds. Chemistry and Application*, Springer-Verlag, Berlin, 2000.
9. M. Krylikowska and Z. Witczak, *Rocz. Chem.*, 1977, **51**, 611.
10. M. A.-F. Elkaschef, F. M. E. Abdel-Megeid, K.-E. M. Mokhtar, and M. F. Elbarnashawi, *Indian J. Chem.*, 1973, **11**, 860.
11. M. R. Mahmoud, A. Y. Soliman, and H. M. Bakeer, *Phosphorus, Sulfur, Silicon*, 1990, **53**, 135.
12. V. Ya. Sosnovskikh and B. I. Usachev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 369 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 383].
13. V. Ya. Sosnovskikh and B. I. Usachev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 1357 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1426].
14. V. Ya. Sosnovskikh, M. A. Barabanov, and B. I. Usachev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1668 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1758].
15. N. S. Prostakov, V. G. Pleshakov, T. S. Seitembetov, D. A. Fesenko, and L. Olubazho Onasan´ya, *Zh. Org. Khim*, 1977, **13**, 1484 [*J. Org. Chem. USSR*, 1977, **13** (Engl. Transl.)].
16. A. A. Fomichev, V. A. Rezakov, V. G. Pleshakov, V. A. Svoren´, M. A. Galiullin, and N. S. Prostakov, *Zh. Org. Khim.*, 1982, **18**, 2591 [*J. Org. Chem. USSR*, 1982, **18** (Engl. Transl.)].
17. V. Ya. Sosnovskikh, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1977 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2087].
18. V. Ya. Sosnovskikh, B. I. Usachev, and I. I. Vorontsov, *J. Org. Chem.*, 2002, **67**, 6738.
19. V. Ya. Sosnovskikh, M. A. Barabanov, and A. Yu. Sizov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 1184 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1280].
20. J. Catalán, F. Fabero, R. M. Claramunt, M. D. Santa Maria, M. C. Foces-Foces, F. H. Cano, M. Martinez-Ripoll, J. Elguero, and R. Sastre, *J. Am. Chem. Soc.*, 1992, **114**, 5039.
21. V. Ya. Sosnovskikh and B. I. Usachev, *Mendeleev Commun.*, 2002, 75.
22. V. Ya. Sosnovskikh and B. I. Usachev, *Synthesis*, 2002, 2341.
23. V. Ya. Sosnovskikh and B. I. Usachev, *Mendeleev Commun.*, 2000, 240.
24. R. Beugelmans and C. Morin, *J. Org. Chem.*, 1977, **42**, 1356.
25. W. Basin´ski and Z. Jerzmanowska, *Roc. Chem.*, 1974, **48**, 2217.
26. Z. Jerzmanowska and W. Basin´ski, *Roc. Chem.*, 1977, **51**, 1791.
27. W. Basin´ski and Z. Jerzmanowska, *Roc. Chem.*, 1976, **50**, 1067.
28. V. Szabó, J. Borbély, E. Theisz, J. Borda, and G. Janzsó, *Tetrahedron*, 1986, **40**, 413.
29. J. Borda, V. Szabó, and J. Borbély, *Acta Chim. Hung.*, 1983, **114**, 103.
30. V. Ya. Sosnovskikh, A. Yu. Sizov, and B. I. Usachev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 1175 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1270].
31. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
32. V. Ya. Sosnovskikh, D. V. Sevenard, B. I. Usachev, and G.-V. Röschenthaler, *Tetrahedron Lett.*, 2003, **44**, 2097.
33. V. Ya. Sosnovskikh, B. I. Usachev, D. V. Sevenard, and G.-V. Röschenthaler, *J. Org. Chem.*, 2003, **68**, 7747.
34. V. Ya. Sosnovskikh, B. I. Usachev, D. V. Sevenard, E. Lork, and G.-V. Röschenthaler, *Tetrahedron Lett.*, 2001, **42**, 5117.
35. V. Ya. Sosnovskikh, B. I. Usachev, D. V. Sevenard, and G.-V. Röschenthaler, *Tetrahedron*, 2003, **59**, 2625.
36. V. Ya. Sosnovskikh and B. I. Usachev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 2109 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 2074].
37. W. B. Whalley, *J. Chem. Soc.*, 1951, 3235.

Received March 31, 2004