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# SYNTHESIS OF 5-POLYFLUOROALKYL-4-(*p*-TOLYL-SULFONYL)PYRAZOLES AND 4-POLYFLUOROALKYL-5-(*p*-TOLYLSULFONYL)PYRIMIDINES FROM 1-DIMETHYLAMINO-2-(*p*-TOLYLSULFONYL)-POLYFLUORO-1-ALKEN-3-ONES

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*1-Dimethylamino-2-(p-tolylsulfonyl)polyfluoro-1-alken-3-ones were obtained from hydrates of 3,3,3-trifluoro-1-(p-tolylsulfonyl)-2-propanone and 3,3,4,4,5,5-hexafluoro-1-(p-tolylsulfonyl)-2-pentanone under conditions of the Vilsmeier-Haack-Arnold reaction. The analogous reaction of 3,3-difluoro-1-(p-tolylsulfonyl)-2-propanone hydrate leads to 3-chloro-1-dimethylamino-4,4-difluoro-2-(p-tolylsulfonyl)-1,3-butadiene. The feasibility of using 1-dimethylamino-2-(p-tolylsulfonyl)-polyfluoro-1-alken-3-ones in reactions with nitrogen binucleophiles has been demonstrated for the regioselective synthesis of pyrazoles and pyrimidines. The structure of 1-phenyl-4-(p-tolylsulfonyl)-5-trifluoromethyl-1H-pyrazole was confirmed by X-ray diffraction structural analysis.*

**Keywords:** 1-arylsulfonyl-1,1-dihydropolyfluoro-2-alkanone, enaminone, pyrazole, pyrimidine, Vilsmeier-Haack-Arnold reaction, X-ray diffraction structural analysis.

Fluoropyrazoles and fluoropyrimidines display a variety of strong biological activities [1-5], which has led to work to develop new methods for the synthesis of such heterocyclic compounds.

The synthetic approaches for the heterocyclic pyrazole system have been studied extensively. The most common approach involves a reaction, in which the three-carbon fragment of a β-dicarbonyl compound or its synthetic equivalent is condensed with the diatomic N–N fragment of hydrazine or its derivative. A problem with this approach is the regioselectivity of the reaction using asymmetric starting compounds since a mixture of N-substituted pyrazoles is formed in most cases [6]. The similar reaction of β-dicarbonyl compounds with a binucleophile possessing an N–C–N fragment leads to the formation of pyrimidines and is also frequently used for the design of these heterocycles [7].

In the present work, we studied the feasibility of using 1-dimethylamino-2-(*p*-tolylsulfonyl)-polyfluoro-1-alken-3-ones **2a,b**, which are the synthetic equivalents of a new type of β-dicarbonyl compounds, namely, 1-arylsulfonyl-2-oxopolyfluoroalkanals **1a,b** for the regioselective synthesis of fluoropyrazoles and fluoropyrimidines. Monoenamines of various 1,3-dicarbonyl compounds (amide vinylogs) have found common use in the synthesis of many heterocyclic systems [8].

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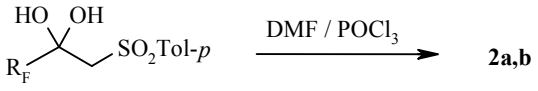
**1a,b** **2a,b**

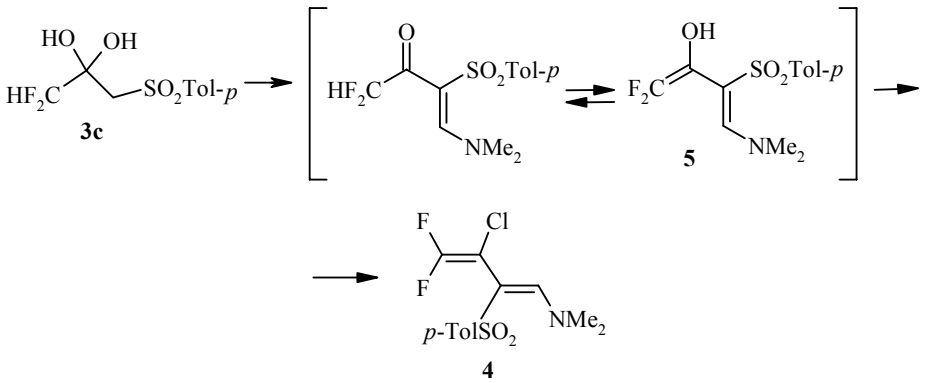
**1, 2 a** $R_F = H(CF_2)_3$, **b** $R_F = CF_3$

Enaminones **2a**,**b** were obtained by the Vilsmeier-Haack-Arnold reaction [9] from 1-arylsulfonyl-1,1-dihydropolyfluoro-2-alkanone hydrates **3a**,**b** [10]. This reaction proceeds at room temperature. The use of ketosulfone hydrate **3c** under analogous conditions leads to a mixture of reaction products.



**3a,b**

**3** **a** $R_F = H(CF_2)_3$, **b** $R_F = CF_3$



**3c** **5** **4**

Heating this mixture to 100°C permitted the isolation of aminodiene **4** as a pure product. Aminodiene **4** is apparently formed as the result of the chlorination of the enolic form of intermediate keto sulfone **5**.

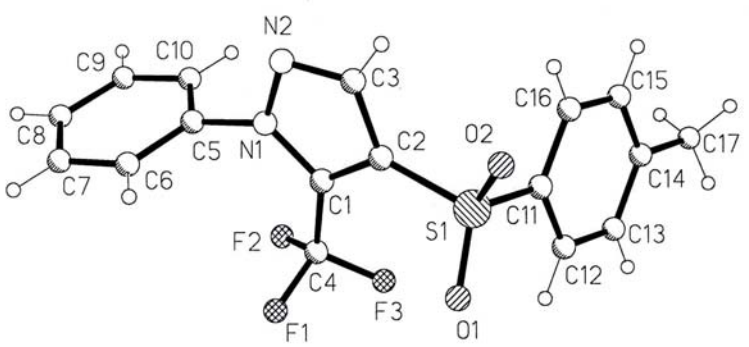
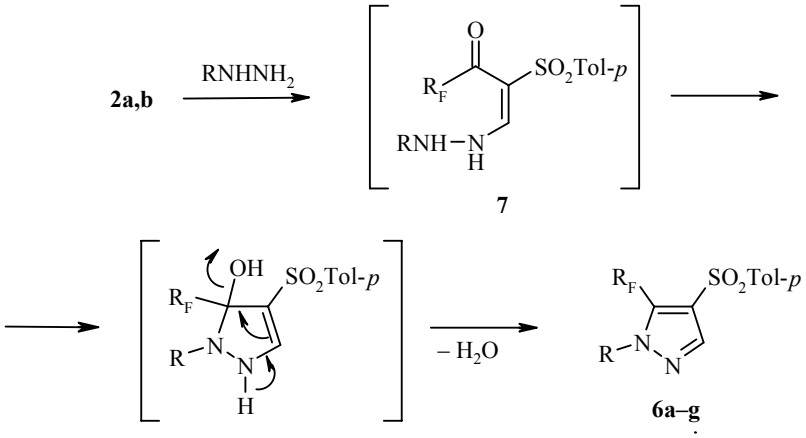



Fig. 1. General view of a molecule of **6d**. Selected bond lengths and angles: $C_{(5)}$–$N_{(1)}$ 1.443(2), $N_{(1)}$–$C_{(1)}$ 1.352(2), $N_{(1)}$–$N_{(2)}$ 1.356(2), $N_{(2)}$–$C_{(3)}$ 1.371(3), $S_{(1)}$–$C_{(2)}$ 1.757(2), $S_{(1)}$–$O_{(1)}$ 1.4251(16), $S_{(1)}$–$O_{(2)}$ 1.4345(17), $S_{(1)}$–$C_{(11)}$ 1.755(2) Å; $C_{(5)}N_{(1)}C_{(1)}$ 129.04(16), $C_{(5)}N_{(1)}N_{(2)}$ 119.2(16), $N_{(1)}N_{(2)}C_{(3)}$ 105.33(17)°.

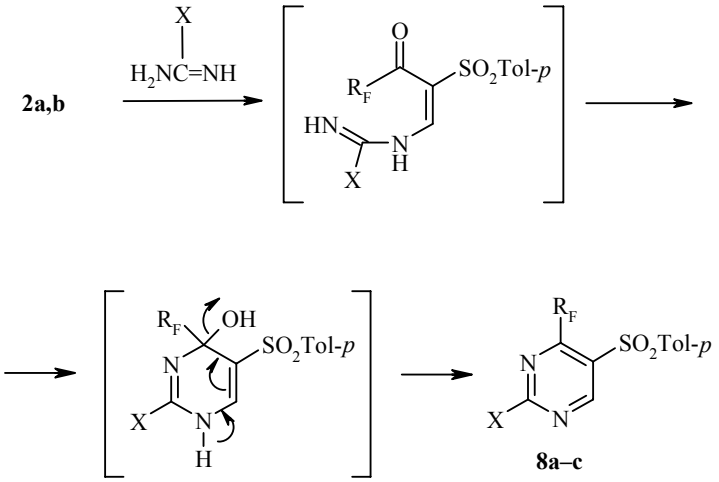
Pyrazoles **6a-g** were obtained by adding the corresponding hydrazine to a solution of enaminone **2a,b** in acetonitrile. The reaction is complete in 2 h at room temperature. This reaction is conveniently monitored by $^{19}F$ NMR spectroscopy of the reaction mixture and the spectra show signals only for one of the two possible regioisomers **6**. The structure of **6d** was unequivocally demonstrated by X-ray diffraction structural analysis. A general view of a molecule of **6d** and the major bond lengths and angles are shown in Fig. 1. The central pyrazole ring $C_{(1)}C_{(2)}C_{(3)}N_{(2)}N_{(1)}$ is virtually planar; the deviation from the mean square plane does not exceed 0.005 Å. Steric hindrance forces benzene rings $C_{(5)}$–$C_{(10)}$ and $C_{(11)}$–$C_{(16)}$ to be twisted almost orthogonally to the central benzene ring; the corresponding dihedral angles are 80.68° and 74.48°.




**6 a** $R_F = H(CF_2)_3$, R = Ph, **b** $R_F = H(CF_2)_3$, R = 2-$ClC_6H_4$, **c** $R_F = H(CF_2)_3$, R = Me,
**d** $R_F = CF_3$, R = Ph, **e** $R_F = CF_3$, R = 2-$ClC_6H_4$, **f** $R_F = CF_3$, R = Me, **g** $R_F = H(CF_2)_3$, R = H

The formation of only one regioisomer suggests that the first step features transamination of enaminone **2** with subsequent intramolecular nucleophilic attack of the carbonyl group carbon by the second nitrogen atom in intermediate **7**, leading to loss of a water molecule and formation of heterocycle **6** [11].

Pyrimidines **8a-c** were obtained using salts of the corresponding amidines as the N–C–N fragment.




**8 a** $R_F = H(CF_2)_3$, X = $NH_2$, **b** $R_F = CF_3$, X = $NH_2$, **c** $R_F = H(CF_2)_3$, X = Me

## EXPERIMENTAL

The $^{1}H$, $^{19}F$, and $^{13}C$ NMR spectra were taken on a Varian VXR-300 spectrometer at 300, 282, and 75 MHz, respectively, for solutions in $CDCl_3$ (**2a,b, 4,** and **6a-g**) and in DMSO-$d_6$ (**8a-c**) with TMS (for the $^{1}H$ and $^{13}C$ NMR spectra) and $C_6F_6$ ($\delta$ = -162.9 ppm relative to $CCl_3F$ for the $^{19}F$ NMR spectra) as the internal standard. The mass spectra were taken on an Agilent 1100 Series mass spectrometer equipped with an Agilent LC\MSD SL dimonomatrix and mass-selective detector. Atmospheric pressure chemical ionization (APCI) was used. The IR spectra were taken on a UR-20 spectrometer. Silica gel 60A 70-230 was used for the column chromatography. All the solvents were initially dried and distilled according to standard procedures.

**Enaminones 2a,b. (General Method)**. A sample of DMF (6 ml) was added to $POCl_3$ (2.8 ml, 30 mmol) and the complex was stirred for 1 h. Then, a solution of keto sulfone hydrate **3a**,**b** (5 mmol) in DMF (6 ml) was added, stirred for 2 h at 20°C, and poured onto ice. The crystalline precipitate was filtered off, washed with water, and dried. The resultant enaminones were used in the subsequent syntheses without further purification. Analytical samples were obtained by crystallization.

**1-Dimethylamino-4,4,5,5,6,6-hexafluoro-2-(*p*-tolylsulfonyl)hex-1-en-3-one (2a)** was obtained in 88% yield; mp 118-120°C (1:4 hexane–ether). IR spectrum (neat), $\nu$, $cm^{-1}$: 1610 (C=C), 1660 (C=O). $^{1}H$ NMR spectrum, $\delta$, ppm (*J*, Hz): 8.26 (1H, s, CH=N); 7.28 and 7.75 (4H, dd, $^{3}J_{HH}$= 8.0, $C_6H_4$); 6.16 (1H, tt, $^{2}J_{HF}$ = 53.0, $^{3}J_{HF}$ = 6.0, $HCF_2$); 3.44 (3H, s, $NCH_3$); 3.04 (3H, s, $NCH_3$); 2.42 (3H, s, $CH_3$). $^{19}F$ NMR spectrum, $\delta$, ppm (*J*, Hz): -118.14 (2F, m, $CF_2$); -133.56 (2F, m, $CF_2$); -133.42 (2F, dm, $J_{FH}$ = 53.0, $HCF_2$). Mass spectrum, *m/z*: 404 $[M]^+$. Found, %: C 44.53; H 3.74; N 3.77; S, 8.07. $C_{15}H_{15}F_6NO_3S$. Calculated, %: C 44.67; H 3.75; N 3.47; S 7.95.

**1-Dimethylamino-4,4,4-trifluoro-3-(*p*-tolylsulfonyl)but-1-en-3-one (2b)** was obtained in 82% yield; mp 155-157°C (methanol). $^{1}H$ NMR spectrum, $\delta$, ppm (*J*, Hz): 8.16 (1H, s, CH=N); 7.25 and 7.73 (4H, dd, $^{3}J_{HH}$ = 8.0, $C_6H_4$); 3.42 (3H, s, $NCH_3$); 2.92 (3H, s, $NCH_3$); 2.40 (3H, s, $CH_3$). $^{19}F$ NMR spectrum, $\delta$, ppm: -73.04 (s, $CF_3$).

**3-Chloro-1-dimethylamino-4,4-difluoro-2-(*p*-tolylsulfonyl)-1,3-butadiene (4).** A sample of $POCl_3$ (2.8 ml, 30 mmol) was added to DMF (6 ml) and the complex was stirred for 1 h. Then, a solution of ketosulfone hydrate **3c** (1.24 g) in DMF (6 ml) was added, maintained for 2 h at 100°C, cooled, and poured onto ice. The crystalline precipitate was filtered off, washed with water, and dried to give **4** in 75% yield; mp 114-116°C (9:1 hexane–ether). $^{1}$NMR spectrum, $\delta$, ppm (*J*, Hz): 7.51 (1H, s, CH=N); 7.26 and 7.72 (4H, dd, $^{3}J_{HH}$ = 8.0, $C_6H_4$); 3.09 (6H, s, $N(CH_3)_2$); 2.41 (3H, s, $CH_3$). $^{19}F$ NMR spectrum, $\delta$, ppm (*J*, Hz): -80.41 (1F, d, $J_{FF}$ = 16.0, CF); -83.27 (1F, d, $J_{FF}$ = 16.0, CF). $^{13}C$ NMR spectrum, $\delta$, ppm (*J*, Hz): 155.45 (dd, $^{2}J_{CF}$ = 290.0, $^{2}J_{CF}$ = 296.0, $CF_2$); 150.39 (d, $^{4}J_{CF}$ = 2.5, =CH); 142.93 (s, $C_{(Ar)}CH_3$); 139.78 (s, $C_{(Ar)}SO_2$); 129.40 (s, $C_{(Ar)}H$); 127.28 (s, $C_{(Ar)}H$); 94.91 (s, =C–$SO_2$); 84.48 (dd, $^{2}J_{CF}$ = 29.0, $^{2}J_{CF}$ = 40.0, =C–Cl); 47.37 (br., $CH_3N$); 37.45 (br., $CH_3N$); 21.54 (s, $CH_{3(Ar)}$). Mass spectrum, *m/z*: 322 $[M]^+$. Found, %: C 48.66; H 4.26; Cl 11.21; N 4.38; S 10.15. $C_{13}H_{14}ClF_2NO_2S$. Calculated, %: C 48.52; H 4.39; Cl 11.02; N 4.35; S, 9.97.

**5-Polyfluoroalkyl-4-(*p*-tolylsulfonyl)pyrazoles 6a-g (General Method)**. Corresponding hydrazine (1 mmol) was added to a solution of **2a**,**b** (1 mmol) in acetonitrile (7 ml) and stirred for 2 h at 20°C. The reaction mixture was filtered and the filtrate was evaporated at 50°C (10-15 mm Hg). The residue was crystallized.

**5-(1,1,2,2,3,3-Hexafluoropropyl)-1-phenyl-4-(*p*-tolylsulfonyl)-1H-pyrazole (6a)** was obtained in 88% yield; mp144-146°C (ethanol). $^{1}H$ NMR spectrum, $\delta$, ppm (*J*, Hz): 8.18 (1H, s, HC=N); 7.33 and 7.86 (4H, dd, $^{3}J_{HH}$ = 8.0, $C_6H_4$); 7.36-7.56 (5H, m, $C_6H_5$); 6.24 (1H, tt, $^{2}J_{HF}$ = 52.0, $^{3}J_{HF}$ = 6.0, $HCF_2$); 2.46 (3H, s, $CH_3$). $^{19}F$ NMR spectrum, $\delta$, ppm (*J*, Hz): -103.71 (2F, m, $CF_2$); -129.61 (2F, m, $CF_2$); -138.74 (2F, dm, $J_{FH}$ = 52.0, $HCF_2$). $^{13}C$ NMR spectrum, $\delta$, ppm (*J*, Hz): 144.89 (s, $C_{(Py)}SO_2$); 142.15 (s, CH=N); 138.70 (s, $C_{(Ar)}CH_3$); 138.47 ($C_{(Ar)}SO_2$); 130.59 (t, $J_{CF}$ = 32.5, $C_{(Py)}CF_2$); 130.48 (s, $C_{(Ph)}H$); 129.85 (s, $C_{(Ar)}H$); 128.67 (s, $C_{(Ar)}H$); 127.91 (s, $C_{(Ph)}H$); 127.23 (s, $C_{(Ph)}H$); 112.52 (tm, $J_{CF}$ = 253.0, $HCF_2\underline{C}F_2CF_2$); 109.60 (tt, $J_{CF}$ = 258.5, $^{2}J_{CF}$ =32.0, $HCF_2CF_2\underline{C}F_2$); 107.67 (tt, $J_{CF}$ = 253.0, $^{2}J_{CF}$ = 29.5, $H\underline{C}F_2CF_2CF_2$); 21.60 (s, $CH_{3(Ar)}$). Mass spectrum, *m/z*: 449.2 $[M]^+$. Found, %: C 50.88; H 3.11; N 6.32; S 7.22. $C_{19}H_{14}F_6N_2O_2S$. Calculated, %: C 50.89; H 3.15; N 6.25; S 7.15.

**1-(2-Chlorophenyl)-5-(1,1,2,2,3,3-hexafluoropropyl)-4-(*p*-tolylsulfonyl)-1H-pyrazole (6b)** was obtained in 83% yield; mp 113-115°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 8.23 (1H, s, CH=N); 7.36 and 7.85 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 7.38-7.54 (4H, m, 2-$ClC_6H_4$); 6.28 (1H, tt, $^2J_{HF}$ = 51.7, $HCF_2$); 2.46 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm (*J*, Hz): $F_A$ -103.95, $F_B$ -108.85 (2F, AB, $J_{FF}$ = 297.0, $CF_2$); $F_A$ -129.58, $F_B$ -130.25 (2F, AB, $J_{FF}$ =285.0, $CF_2$); -138.53 (2F, m, $HCF_2$).

**5-(1,1,2,2,3,3-Hexafluoropropyl)-1-methyl-4-(*p*-tolylsulfonyl)-1H-pyrazole (6c)** was obtained in 68% yield; mp 124-126°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 8.09 (1H, s, CH=N); 7.31 and 7.80 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 6.30 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 6.0, $HCF_2$); 3.99 (3H, s, $NCH_3$); 2.42 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm (*J*, Hz): -107.59 (2F, m, $CF_2$); -132.28 (2F, m, $CF_2$); -138.32 (2F, dm, $^2J_{FH}$ = 52.0, $HCF_2$). $^{13}$C NMR spectrum, δ, ppm (*J*, Hz): 144.63 (s, $C_{(Py)}SO_2$); 138.56 (t, $J_{CF}$ = 31.5, $C_{(Py)}CF_2$); 138.33 (s, $C_{(Ar)}CH_3$); 136.58 (s, CH=N); 129.69 ($C_{(Ar)}H$); 127.72 (s, $C_{(Ar)}H$); 125.27 (s, $C_{(Ar)}SO_2$); 112.20 (tt, $J_{CF}$ = 252.0, $^2J_{CF}$ = 30.5, $HCF_2CF_2\underline{C}F_2$); 110.33 (tm, $J_{CF}$ = 263.0, $^2J_{CF}$ = 33.0, $HCF_2\underline{C}F_2CF_2$); 108.04 (tt, $J_{CF}$ = 253.5, $^2J_{CF}$ = 29.0, $H\underline{C}F_2CF_2CF_2$); 40.18 (s, $NCH_3$); 21.53 (s, $CH_{3(Ar)}$).

**1-Phenyl-4-(*p*-tolylsulfonyl)-5-trifluoromethyl-1H-pyrazole (6d)** was obtained in 68% yield; mp 116°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 8.19 (1H, s, CH=N); 7.36 and 7.88 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 7.38-7.56 (5H, m, $C_6H_5$); 2.45 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm: -55.49 (s, $CF_3$).

**1-(2-Chlorophenyl)-4-(*p*-tolylsulfonyl)-5-trifluoromethyl-1H-pyrazole (6e)** was obtained in 63% yield; mp 93-95°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 8.22 (1H, s, CH=N); 7.36 and 7.88 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 7.38-7.57 (4H, m, 2-$ClC_6H_4$); 2.45 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm: -57.32 (s, $CF_3$).

**1-Methyl-4-(*p*-tolylsulfonyl)-5-trifluoromethyl-1H-pyrazole (6f)** was obtained in 61% yield; mp 162-164°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 8.04 (1H, s, CH=N); 7.31 and 7.82 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 3.97 (3H, s, $NCH_3$); 2.45 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm: -61.56 (s, $CF_3$).

**5-(1,1,2,2,3,3-Hexafluoropropyl)-4-(*p*-tolylsulfonyl)-1H-pyrazole (6g).** Hydrazine sulfate (1 mmol) and $K_2CO_3$ (2 mmol) were added to a solution of enaminone **2a** (1 mmol) in acetonitrile (7 ml), heated at reflux with stirring for 8 h, filtered, and evaporated to dryness. The residue was purified by chromatography using ethyl acetate as the eluent to give pyrazole **6g** in 55% yield as a yellow oil, $R_f$ 0.9 (Silufol UV-254 plate, ethyl acetate as eluent, developed with iodine vapor). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 11.53 (1H, br. s, NH); 8.30 (1H, s, CH=N); 7.31 and 7.80 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 6.29 (1H, tt, $^2J_{HF}$ = 52.5, $^3J_{HF}$ = 6.0, $HCF_2$); 2.46 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm (*J*, Hz): -107.32 (2F, m, $CF_2$); -131.94 (2F, m, $CF_2$); -138.14 (2F, dm, $^2J_{FH}$ = 52.5, $HCF_2$).

**4-Polyfluoroalkyl-5-(*p*-tolylsulfonyl)pyrimidines 8a-c (General Method)**. Guanidine hydrochloride (in the case of **8a**,**b**) or acetamidine hydrochloride (in the case of **8c**) (1 mmol) and $K_2CO_3$ (2 mmol) were added to a solution of enaminone **2a**,**b** in acetonitrile (7 ml). The reaction mixture was heated at reflux with stirring for 2 h, cooled, and treated as in the above procedure.

**2-Amino-4-(1,1,2,2,3,3-hexafluoropropyl)-5-(*p*-tolylsulfonyl)pyrimidine (8a).** The reaction mixture was filtered and the filtrate was evaporated to dryness to give **8a** in 95% yield; mp 217-219°C (acetonitrile). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 9.14 (1H, s, CH=N); 8.46 (2H, br. s, $NH_2$); 7.41 and 7.78 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 7.32 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 6.0, $HCF_2$); 2.38 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm (*J*, Hz): -107.05 (2F, m, $CF_2$); -130.39 (2F, m, $CF_2$); -137.02 (2F, dm, $^2J_{FH}$ = 52.0, $HCF_2$). Mass spectrum, *m/z*: 398 $[M]^+$.

**2-Amino-5-(*p*-tolylsulfonyl)-4-trifluoromethylpyrimidine (8b)**. The precipitate of **8b** formed in the reaction mixture was filtered off, washed on the filter with water, and dried to give **8b** in 84% yield; mp 260-262°C (acetonitrile). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 9.09 (1H, s, CH=N); 8.43 (2H, br. s, $NH_2$); 7.41 and 7.78 (4H, dd, $^3J_{HH}$ = 8.0, $C_6H_4$); 2.38 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm: -64.36 (s, $CF_3$).

**2-Methyl-4-(1,1,2,2,3,3-hexafluoropropyl)-5-(*p*-tolylsulfonyl)pyrimidine (8c).** The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was crystallized to give **8c** in 81% yield; mp 110-112°C (ethanol). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 9.68 (1H, s, CH=N); 7.47 and 7.87 (4H, dd,

$^3J_{HH}$ =8.0, $C_6H_4$); 7.10 (1H, tt, $^2J_{HF}$ = 51.5, $^3J_{HF}$ = 6.0, $HCF_2$); 2.84 (3H, s, $CH_3$); 2.40 (3H, s, $CH_3$). $^{19}$F NMR spectrum, δ, ppm (*J*, Hz): -106.81 (2F, m, $CF_2$); -129.30 (2F, m, $CF_2$); -137.24 (2F, dm, $^2J_{FH}$= 51.5, $HCF_2$).

**X-Ray Diffraction Structural Analysis of a Monocrystal of 6d** grown from absolute ethanol (0.38×0.25×0.20 mm) at room temperature on an automatic Bruker Apex II CCD diffractometer using MoKα radiation, $\lambda = 0.71069$ Å, $\theta_{max} = 31°$, sphere segment $-12 \le h \le 12$, $-14 \le k \le 13$, $-15 \le l \le 14$. We collected 10,339 reflections (5214 independent reflections, $R_{int} = 0.0197$). The unit cell parameters of the triclinic crystals of **6d** are as follows: $a = 8.7461(2)$, $b = 10.1910(2)$, $c = 10.5604(2)$ Å, $V = 856.47(3)$ Å$^3$, $M = 435.03$, $Z = 2$, $d_{calc} = 1.421$ g/cm$^3$, $\mu = 2.32$ cm$^{-1}$, $F(000) = 376$, space group *P*-1 (No. 2). The structure was solved by the direct method and refined by the method of least squares in the full-matrix anisotropic approximation using the SHELX897 and SHELXL97 programs [12, 13]. A total of 5214 reflections were used in the refinement (3684 reflections with $I > 2\sigma(I)$ and 232 refined parameters, the number of reflections per parameter was 22.47). All the hydrogen atoms were found in the electron density difference map and placed in the refinement with fixed positional and temperature parameters. The following weighting scheme was used: $\omega = 1/[\sigma^2(Fo^2) + (0.1006P)^2 + 0.8932P]$, where $P = (Fo^2 + 2Fc^2)/3$. The final $R_1 = 0.0544$ and $wR_2 = 0.0766$, GOOF = 0.708. The residual electron density from the Fourier difference map was -0.363 and 0.541 e/Å$^3$. The full set of X-ray diffraction structural data for **6d** was deposited in the Cambridge Crystallographic Data Center (CCDC 645235).

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