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# Synthesis of New 2-(Alkenylsulfanyl)pyrimidine Derivatives

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**Abstract**—Isothiuronium salts prepared by treatment of allyl bromide, 2,3- and 1,3-dichloropropenes, and 1,3-dichlorobut-2-ene with thiourea reacted with pentane-2,4-dione and 4,4,4-trifluoro-1-(thiophen-2-yl)-butane-1,3-dione to afford new pyrimidine derivatives, 2-(alkenylsulfanyl)-4,6-dimethyl- and 2-(alkenylsulfanyl)-4-(thiophen-2-yl)-6-(trifluoromethyl)pyrimidines.

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2-(Organylsulfanyl)pyrimidine derivatives are very significant among diverse practically important compounds of the pyrimidine series. A combination of pharmacophoric pyrimidine and sulfanyl moieties in a single molecule gives rise to versatile biological activity. 2-(Organylsulfanyl)-substituted pyrimidines were found to act as enzyme inhibitors and antagonists of some receptors affecting nucleic acids synthesis [1, 2] and cell growth, proliferation, and metabolism [3], which leads to the appearance of antiviral (including anti-HIV) [4, 5], anticancer [3, 6–8], antidiabetic [9], and antiphlogistic activity [8].

Sulfanylpyrimidine derivatives are used as model structures in theoretical studies [10] and are also important and often indispensable reagents in the chemistry of pyrimidines. The synthesis of biologically active pyrimidinamines based on the transformations of sulfanylpyrimidine is well known [11–18]. Selective cross-couplings involving a sulfanylpyrimidine fragment were reported [19], and reactions were described [20, 21] where pyrimidine moiety behaves as a leaving group providing an approach to selective preparation of difficultly accessible polysubstituted alkenes.

Taking into account high importance of organylsulfanyl-substituted pyrimidines, the synthesis of their new derivatives is a topical goal.

In this paper we describe the synthesis of previously unknown 2-(alkenylsulfanyl)pyrimidine derivatives necessary for the preparation of functionalized fused pyrimidines which are promising from the viewpoint of their biological activity.

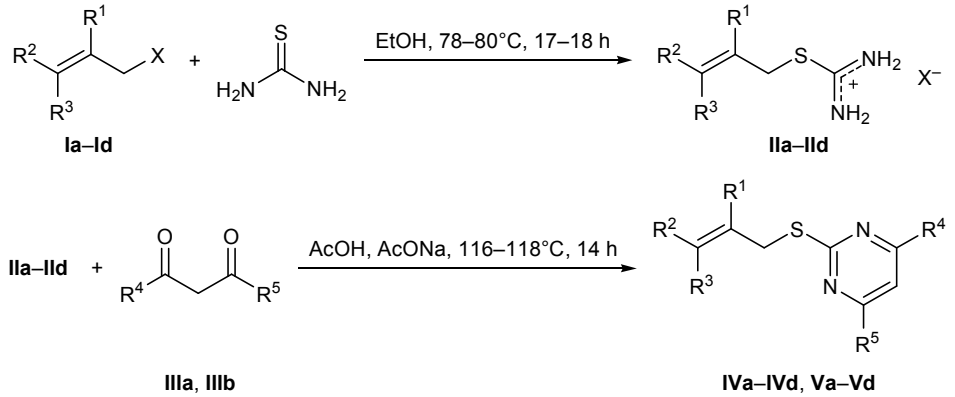
Sulfanyl-substituted pyrimidines were synthesized in two steps (Scheme 1). Preliminarily, allyl bromide (**Ia**), 2,3-dichloropropene (**Ib**), 1,3-dichloropropene (**Ic**), and 1,3-dichlorobut-2-ene (**Id**) were reacted with thiourea to obtain isothiuronium salts **IIa**–**IId** in 82–97% yield. The $^1$H and $^{13}$C NMR spectra of **IIa**–**IId** contained proton and carbon signals from the alkenyl groups, a signal from the $NH_2$ protons at δ 8.4–9.4 ppm, and C=S carbon signal at $\delta_C$ 169–170 ppm.

The target sulfanyl-substituted pyrimidines **IVa**–**IVd** and **Va**–**Vd** were obtained by reaction of isothiuronium salts **IIa**–**IId** with 1,3-diketones **IIIa** and **IIIb**. The maximum yields of **IVa**–**IVd** and **Va**–**Vd** (57–88%) were achieved by heating the reactants in boiling acetic acid in the presence of sodium acetate.

Isothiuronium salts **IIc** and **IId** and 2-sulfanyl-substituted pyrimidines **IVc**, **IVd**, **Vc**, and **Vd** derived from 1,3-dichloropropene (**Ic**) and 1,3-dichlorobut-2-ene (**Id**) were obtained as mixtures of *E* and *Z* isomers. The *E*/*Z* isomer ratios for compounds **IIc**, **IVc**, **Vc** and **IId**, **IVd**, **Vd** were estimated at 1:1 and 1:9, respectively, on the basis of their $^1$H NMR spectra, and these ratios coincided with the isomeric compositions of initial dichloroalkenes **Ic** and **Id**.

Compounds **IVa**–**IVd** were isolated as viscous liquids, and 4-(2-thienyl)-6-trifluoromethyl derivatives **Va**–**Vd** are low melting crystalline substances. Their structure was unambiguously proved by spectral methods and elemental analysis. Signals in the NMR spectra of **IVa**–**IVd** and **Va**–**Vd** were assigned, and the

**Scheme 1.**




**I**, **II**, X = Br, $R^1 = R^2 = R^3 = H$ (**a**); X = $R^1$ = Cl, $R^2 = R^3 = H$ (**b**); X = $R^2$ = Cl, $R^1 = R^3 = H$ (**c**); X = $R^2$ = Cl, $R^1$ = H, $R^3$ = Me (**d**); **III**, $R^4 = R^5$ = Me (**a**); $R^4 = CF_3$, $R^5$ = thiophen-2-yl (**b**); **IV**, $R^4 = R^5$ = Me: $R^1 = R^2 = R^3 = H$ (**a**); $R^1$ = Cl, $R^2 = R^3 = H$ (**b**); $R^1 = R^3$ = H, $R^2$ = Cl (**c**); $R^1$ = H, $R^2$ = Cl, $R^3$ = Me (**d**); **V**, $R^4 = CF_3$, $R^5$ = thiophen-2-yl: $R^1 = R^2 = R^3 = H$ (**a**); $R^1$ = Cl, $R^2 = R^3 = H$ (**b**); $R^1 = R^3$ = H, $R^2$ = Cl (**c**); $R^1$ = H, $R^2$ = Cl, $R^3$ = Me (**d**).

structure of *Z* and *E* isomers was determined, using two-dimensional NMR techniques.

In the $^1H$ and $^{13}C$ NMR spectra of **IVa–IVd** and **Va–Vd** we observed signals belonging to protons and carbon atoms in both alkenyl fragments and substituents in the pyrimidine ring. The 5-H proton in the pyrimidine ring gave rise to a singlet at δ 6.70 ppm for dimethyl-substituted derivatives **IVa–IVd** or δ 7.45–7.60 ppm for trifluoromethyl derivatives **Va–Vd**, indicating 2,4,6-substitution pattern. Signals from the C–S carbon atom in the $^{13}C$ NMR spectra of isothiuronium salts **IIa–IId** appeared in the same region as those belonging to $C^2$ in the spectra of pyrimidines **IV** and **V** ($\delta_C$ 169–173 ppm). The transformation of the carbonyl carbon atoms of initial diketones **IIIa** and **IIIb** into $C^4$ and $C^6$ in the pyrimidine ring of **IV** and **V** was accompanied by considerable upfield of the corresponding signals.

Thus, we have synthesized new pyrimidine derivatives which attract interest as substrates for further transformations due to the presence of alkenylsulfanyl substituents in their molecules.

## EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS spectrometer. The $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz, respectively, using hexamethyldisiloxane as internal reference. The purity of initial compounds was checked, and the products were analyzed, by GLC on an LKhM 80-MD-2 chromatograph equipped with a 2000 × 3-mm column packed with 5% of XE-60 on Chromaton N-AW-HMDS; oven temperature programming from 30 to 230°C at a rate of 12 deg/min; carrier gas helium. The mass spectra were obtained on a Shimadzu GCMS-QP5050A instrument (SPB-5 column, 60000 × 0.25 mm, film thickness 0.25 μm; injector temperature 250°C; carrier gas helium, flow rate 0.7 mL/min; oven temperature programming from 60 to 260°C at a rate of 15 deg/min; detector temperature 250°C; quadrupole mass analyzer; electron impact, 70 eV; ion source temperature 200°C; a.m.u. range 34–650).

***S*-Allylisothiuronium bromide (IIa).** A mixture of 12.10 g (0.10 mol) of allyl bromide (**Ia**), 7.61 g (0.10 mol) of thiourea, and 60 mL of ethanol was heated for 20 h under reflux. The mixture was cooled and diluted with 60 mL of diethyl ether, and the precipitate was filtered off, washed with diethyl ether, and dried under reduced pressure. Yield 19.17 g (97%), mp 74–76°C. IR spectrum (KBr), ν, $cm^{-1}$: 3307, 3254 (NH); 1639 (C=C); 681 (C–S). $^1H$ NMR spectrum ($D_2O$), δ, ppm: 3.83 d.d (2H, $CH_2S$, $^3J$ = 6.5, $^4J$ = 1.1 Hz), 5.32 m (1H, =$CH_2$, $^3J_{cis}$ = 10.2, $^2J$ = 1.1, $^4J$ = 1.1 Hz), 5.43 m (1H, =$CH_2$, $^3J_{trans}$ = 17.1, $^2J$ = 1.1, $^4J$ = 1.1 Hz), 5.94 m (1H, =CH, $^3J$ = 6.5, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.1 Hz), 8.44 br.s ($NH_2$). $^{13}C$ NMR spectrum ($D_2O$), $\delta_C$, ppm: 33.1 ($SCH_2$), 119.9 ($CH_2$=), 131.6 (CH=), 169.3 (SCN). Found, %: C 24.57; H 4.61; Br 40.62; N 14.19; S 16.75. $C_4H_9BrN_2S$. Calculated, %: C 24.38; H 4.60; Br 40.54; N 14.21; S 16.27.

***S*-(2-Chloroprop-2-en-1-yl)isothiuronium chloride (IIb).** A mixture of 22.19 g (0.20 mol) of 2,3-dichloroprop-1-ene (**Ib**) and 15.22 g (0.20 mol) of thiourea in 120 mL of ethanol was heated for 17 h under

reflux, and the mixture was treated as described above. Yield 33.60 g (90%), mp 135–137°C. IR spectrum (KBr), ν, $cm^{-1}$: 3274, 3187 (N–H); 1656 (C=C); 721 (C–Cl); 629 (C–S). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 4.45 s (2H, $SCH_2$), 5.46 d and 5.81 d (1H each, $=CH_2$, $^2J$ = 1.3 Hz), 9.41 br.s and 9.54 br.s (2H each, $NH_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 37.9 ($CH_2S$), 118.1 ($=CH_2$), 135.6 (=CCl), 168.6 (SCN). Found, %: C 25.61; H 4.27; Cl 37.86; N 15.07; S 17.24. $C_4H_8Cl_2N_2S$. Calculated, %: C 25.68; H 4.31; Cl 37.90; N 14.97; S 17.14.

***S*-(3-Chloroprop-2-en-1-yl)isothiuronium chloride (IIc,** a mixture of *Z* and *E* isomers**).** A mixture of 5.55 g (0.05 mol) of 1,3-dichloroprop-1-ene (**Ic**) and 3.85 g (0.05 mol) of thiourea in 30 mL of ethanol was heated for 12 h under reflux. The mixture was cooled and diluted with 50 mL of diethyl ether, and compound **IIc** (*E*/*Z* isomer mixture) separated as a yellow oily substance. It was isolated by decanting and dried under reduced pressure. Yield 8.51 g (91%). IR spectrum (film), ν, $cm^{-1}$: 3289, 3192 (N–H); 1649 (C=C); 707 (C–Cl); 675 (C–S). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: *Z* isomer: 4.07 d (2H, $CH_2S$, $^3J$ = 7.7 Hz), 6.12 d.t (1H, =CH, $^3J$ = 7.0, 7.7 Hz), 6.61 d (1H, =CHCl, $^3J$ = 7.0 Hz), 9.40 br.s (4H, $NH_2$); *E* isomer: 4.05 d (2H, $CH_2S$, $^3J$ = 7.7 Hz), 6.03 d.t (1H, =CH, $^3J$ = 13.2, 7.7 Hz), 6.73 d (1H, =CHCl, $^3J$ = 13.2 Hz), 9.40 br.s (4H, $NH_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: *Z* isomer: 30.6 ($CH_2S$), 122.8 (=CHCl), 128.1 (=CH), 169.3 (SCH); *E* isomer: 27.6 ($CH_2S$), 124.1 (=CHCl), 125.4 (=CH), 169.8 (SCN). Found, %: C 25.66; H 4.17; Cl 32.31; N 15.01; S 17.18. $C_4H_8Cl_2N_2S$. Calculated, %: C 25.68; H 4.31; Cl 37.90; N 14.97; S 17.14.

***S*-(3-Chlorobut-2-en-1-yl)isothiuronium chloride (IId**, a mixture of *Z* and *E* isomers**).** A mixture of 6.25 g (0.05 mol) of 1,3-dichlorobut-2-ene (**Id**) and 3.85 g (0.50 mol) of thiourea in 30 mL of ethanol was heated for 9.5 h under reflux. The mixture was then treated as described above for the synthesis of **IIa**. Yield 8.28 g (82%), mp 121–122°C. IR spectrum (KBr), ν, $cm^{-1}$: 3206 (N–H), 1656 (C=C), 716 (C–Cl), 700 (C–S). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.14 s (3H, $CH_3$, *Z*), 2.16 d (3H, $CH_3$, *E*), 3.97 d (2H, $CH_2S$, *Z*, $^3J$ = 7.5 Hz), 4.03 d (2H, $CH_2S$, *E*, $^3J$ = 7.5 Hz), 5.87 t (1H, =CH, *Z*, $^3J$ = 7.5 Hz), 5.72 t (1H, =CH, *E*, $^3J$ = 7.5 Hz), 9.39 br.s (4H, $NH_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: *Z* isomer: 25.8 ($CH_3$), 29.0 ($CH_2S$), 119.2 (=CH), 135.9 (=CCl), 169.7 (SCN). Found, %: C 30.07; H 5.10; Cl 35.00; N 14.06; S 16.41. $C_5H_{10}Cl_2N_2S$. Calculated, %: C 29.86; H 5.01; Cl 35.26; H 13.93; S 15.94.

**4,6-Dimethyl-2-(prop-2-en-1-ylsulfanyl)pyrimidine (IVa).** A mixture of 2.50 g (0.013 mol) of salt **IIa**, 2.08 g (0.025 mol) of sodium acetate, and 2.54 g (0.025 mol) of acetylacetone (**IIIa**) in 20 mL of glacial acetic acid was heated for 14 h under reflux. The mixture was cooled to room temperature and filtered, the precipitate was washed on a filter with glacial acetic acid, and acetic acid was distilled off from the filtrate under reduced pressure (40 mm). The dark brown residue was dissolved in water, the product was extracted into methylene chloride (3×20 mL), the extract was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure. Yield 1.89 g (83%), light yellow liquid, bp 114–115°C (2 mm). IR spectrum (film), ν, $cm^{-1}$: 3082–3057, 3008–2923 (C–H); 1582 (C=C). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (6H, $CH_3$), 3.80 d (2H, $SCH_2$, $^3J$ = 6.7 Hz), 5.07 d.d (1H, $=CH_2$, $^3J_{cis}$ = 10.4, $^2J$ = 1.3 Hz), 5.28 d.d (1H, $=CH_2$, $^3J_{trans}$ = 17.0, $^2J$ = 1.3 Hz), 5.96 m (1H, =CH, $^3J_{cis}$ = 10.4, $^3J_{trans}$ = 17.0, $^3J$ = 6.7 Hz), 6.66 s (1H, 5-H). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 23.7 ($CH_3$), 33.6 ($=CH_2$), 115.5 (=CH), 133.9 ($C^5$), 166.8 ($C^4$, $C^6$), 170.6 ($C^2$). Mass spectrum: *m*/*z* 180 $[M]^+$. Found, %: C 59.88; H 6.72; N 15.60; S 17.68. $C_9H_{12}N_2S$. Calculated, %: C 59.96; H 6.71; N 15.54; S 17.79.

**2-(2-Chloroprop-2-en-1-ylsulfanyl)-4,6-dimethylpyrimidine (IVb)** was synthesized in a similar way from 2.50 g (0.013 mol) of compound **IIb** and 2.67 g (0.027 mol) of acetylacetone (**IIIa**). Yield 2.53 g (88%), light yellow liquid, bp 117–120°C (2 mm). IR spectrum (film), ν, $cm^{-1}$: 3055, 2959–2852 (C–H); 1583, 1536 (C=C); 765 (C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (6H, $CH_3$), 4.08 s (2H, $CH_2S$), 5.24 s and 5.54 s (2H, $=CH_2$), 6.69 s (1H, 5-H). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 23.7 ($CH_3$), 38.1 ($CH_2S$), 114.4 ($=CH_2$), 115.9 ($C^5$), 138.2 (=CCl), 167.1 ($C^4$, $C^6$), 169.5 ($C^2$). Mass spectrum: *m*/z 215 $[M]^+$. Found, %: C 50.38; H 5.11; Cl 16.72; N 13.21; S 14.53. $C_9H_{11}ClN_2S$. Calculated, %: C 50.34; H 5.16; Cl 16.51; N 13.05; S 14.93.

**2-(3-Chloroprop-2-en-1-ylsulfanyl)-4,6-dimethylpyrimidine (IVc**, a mixture of *Z* and *E* isomers**)** was synthesized as described above for **IVa** from 2.53 g (0.014 mol) of salt **IIc** and 2.70 g (0.027 mol) of acetylacetone (**IIIa**). Yield 2.32 g (81%). Light yellow liquid, bp 122–123°C (2 mm). IR spectrum (film), ν, $cm^{-1}$: 3063, 2960–2924 (C–H); 1583, 1536 (C=C); 765

(C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (6H, $CH_3$), 3.77 d (2H, $CH_2S$, *Z*, $^3J$ = 7.6 Hz), 3.94 d (2H, $CH_2S$, *E*, $^3J$ = 6.9 Hz), 6.05 d.t (1H, =CH, *E*, $^3J$ = 6.9, 13.2 Hz), 6.07 d.t (1H, =CH, *Z*, $^3J$ = 7.6, 7.2 Hz), 6.10 d (1H, ClCH=, *E*, $^3J$ = 13.2), 6.24 d (1H, ClCH=, *Z*, $^3J$ = 7.2 Hz), 6.68 s and 6.69 s (1H each, 5-H, *E*, *Z*). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 23.7 ($CH_3$), 27.1 ($CH_2S$, *E*), 30.6 ($CH_2S$, *Z*), 115.6 (=CH, *E*), 115.8 (=CH, *Z*), 120.1 (ClCH=, *E*), 120.4 (ClCH=, *Z*), 127.9 ($C^5$, *E*), 129.2 ($C^5$, *Z*), 166.9 ($C^4$, $C^6$), 169.7 ($C^2$, *Z*), 170.2 ($C^2$, *E*). Mass spectrum: *m*/*z* 214 $[M]^+$. Found, %: C 50.33; H 5.28; Cl 15.97; N 13.00; S 14.88. $C_9H_{11}ClN_2S$. Calculated, %: C 50.34; H 5.16; Cl 16.51; N 13.05; S 14.93.

**2-(3-Chlorobut-2-en-1-ylsulfanyl)-4,6-dimethylpyrimidine (IVd,** a mixture of *Z* and *E* isomers**)** was synthesized in a similar way from 2.50 g (0.012 mol) of salt **IId** and 2.49 g (0.025 mol) of acetylacetone (**IIIa**). Yield 2.48 g (87%), light yellow liquid, bp 128–129°C (2 mm). IR spectrum (film), ν, cm$^{-1}$: 2921 (C–H); 1582, 1536 (C=C); 765 (C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 s (3H, $CH_3CCl$=, *E*), 2.18 s (3H, $CH_3CCl$=, *Z*), 2.38 s (6H, $CH_3$), 3.77 d (2H, $SCH_2$, *E*, $^3J$ = 8.1 Hz), 3.89 d (2H, $SCH_2$, *Z*, $^3J$ = 7.2 Hz), 5.74 t (1H, =CH, *Z*, $^3J$ = 7.2 Hz), 5.85 t (1H, =CH, *E*, $^3J$ = 8.1 Hz), 6.67 s (1H, 5-H, *Z*), 6.68 s (1H, 5-H, *E*). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 23.8 ($CH_3$), 26.1 ($CH_3SCl$=), 29.0 ($CH_2S$, *E*), 29.1 ($CH_2S$, *Z*), 115.6 ($C^5$, *Z*), 115.8 ($C^5$, *E*), 121.9 (=CH, *Z*), 123.5 (=CH, *E*), 132.8 (CCl=), 167.0 ($C^4$, $C^6$), 170.8 ($C^2$). Mass spectrum: *m*/*z* 228 $[M]^+$. Found, %: C 52.60; H 5.88; Cl 15.36; N 12.22; S 13.92. $C_{10}H_{13}ClN_2S$. Calculated, %: C 52.51; H 5.73; Cl 15.50; N 12.25; S 14.02.

**2-(Prop-2-en-1-ylsulfanyl)-4-(thiophen-2-yl)-6-(trifluoromethyl)pyrimidine (Va)** was synthesized as described above for compound **IVa** from 2.50 g (0.013 mol) of salt **IIa** and 2.82 g (0.013 mol) of compound **IIIb**. Yield 2.93 g (77%), mp 38–40°C. IR spectrum (KBr), ν, cm$^{-1}$: 3085, 2953–2851 (C–H); 1663, 1583, 1531 (C=C); 1432, 1404, 1388 (C–F). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 d.t (2H, $CH_2S$, $^3J$ = 7.0, $^4J$ = 1.1 Hz), 5.13 d.d.t (1H, =$CH_2$, $^3J_{cis}$ = 10, $^2J$ = 1.1, $^4J$ = 1.1 Hz), 5.36 d.d.t (1H, =$CH_2$, $^3J_{trans}$ = 17, $^2J$ = $^4J$ = 1.1 Hz), 5.98 d.d.t (1H, =CH, $^3J_{trans}$ = 17.0, $^3J_{cis}$ = 10.0, $^3J$ = 7.0 Hz), 7.13 d.d (1H, 4′-H, $^3J$ = 5.0, 3.8 Hz), 7.55 d (1H, 5′-H, $^3J$ = 5.0 Hz), 7.78 d (1H, 3′-H, $^3J$ = 3.8 Hz), 7.42 s (1H, 5-H). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 34.0 ($CH_2S$), 105.9 ($C^5$), 118.2 (=$CH_2$), 120.4 q ($CF_3$, $^1J_{CF}$ = 275.7 Hz), 128.7 ($C^{4'}$), 129.1 ($C^{3'}$), 131.9 (=CH), 133.0 ($C^{5'}$), 141.0 ($C^{2'}$), 156.2 q ($C^6$, $^2J_{CF}$ = 36.0 Hz), 161.1 ($C^4$), 173.3 ($C^2$). Mass spectrum: *m*/*z* 302 $[M]^+$. Found, %: C 47.78; H 3.11; N 9.10; S 21.65. $C_{12}H_9F_3N_2S_2$. Calculated, %: C 47.67; H 3.00; N 9.27; S 21.21.

**2-(2-Chloroprop-2-en-1-ylsulfanyl)-4-(thiophen-2-yl)-6-(trifluoromethyl)pyrimidine (Vb)** was synthesized as described above for **IVa** from 2.00 g (0.011 mol) of **IIb** and 2.38 g (0.011 mol) of **IIIb**. Yield 2.62 g (57%), mp 91–93°C. IR spectrum (KBr), ν, cm$^{-1}$: 3094, 2994–2918 (C–H); 1665, 1592, 1531 (C=C); 1143, 1127 (C–F); 728 (C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 4.12 s (2H, $CH_2S$), 5.30 d and 5.63 d (1H each, =$CH_2$, $^2J$ = 1.0 Hz), 7.17 d.d (1H, 4′-H, $^3J$ = 5.0, 3.8 Hz), 7.47 s (1H, 5-H), 7.60 d (1H, 5′-H, $^3J$ = 5.0 Hz), 7.82 d (1H, 3′-H, $^3J$ = 3.8 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 38.6 ($CH_2S$), 106.4 q ($C^5$, $^3J_{CF}$ = 2.1 Hz), 115.2 (=$CH_2$), 120.4 q ($CF_3$, $^1J_{CF}$ = 275.5 Hz), 128.8 ($C^{4'}$), 129.4 ($C^{3'}$), 132.1 ($C^{5'}$), 137.3 (=CCl), 140.8 ($C^{2'}$), 155.9 q ($C^6$, $^2J_{CF}$ = 36.0 Hz), 161.3 ($C^4$), 172.3 ($C^2$). Mass spectrum: *m*/*z* 336 $[M]^+$. Found, %: C 42.93; H 2.27; N 8.31; S 19.13. $C_{12}H_8ClF_3N_2S_2$. Calculated, %: C 42.80; H 2.39; N 8.32; S 19.04.

**2-(3-Chloroprop-2-en-1-ylsulfanyl)-4-(thiophen-2-yl)-6-(trifluoromethyl)pyrimidine (Vc)** was synthesized in a similar way from 2.00 g (0.011 mol) of isothiuronium salt **IIc** and 2.38 g (0.011 mol) of compound **IIIb**. Yield 2.10 g (58%), mp 79°C. IR spectrum (KBr), ν, cm$^{-1}$: 3086–2938 (C–H); 1627, 1581, 1538 (C=C); 1182, 1147, 1116 (C–F); 725 (C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 3.83 d (2H, $CH_2S$, *Z*, $^3J$ = 7.7 Hz), 4.00 d (2H, $CH_2S$, *E*, $^3J$ = 6.5 Hz), 6.07 d.t (1H, =CH, *E*, $^3J$ = 6.5, 13.2 Hz), 6.15 d.t (1H, =CH, *Z*, $^3J$ = 7.1, 7.7 Hz), 6.18 d (1H, ClCH=, *Z*, $^3J$ = 7.1 Hz), 6.37 d (1H, ClCH=, *E*, $^3J$ = 13.2 Hz), 7.17 d.d (1H, 4′-H, *Z*, $^3J$ = 2.1, 3.8 Hz), 7.18 d.d (1H, 4′-H, *E*, $^3J$ = 2.1, 3.8 Hz), 7.47 s (1H, 5-H, *Z*), 7.48 s (1H, 5-H, *E*), 7.59 d (1H, 5′-H, *Z*, $^3J$ = 3.8 Hz), 7.60 d (1H, 5′-H, *E*, $^3J$ = 3.8 Hz), 7.82 d (1H, 3′-H, *Z*, $^3J$ = 2.1 Hz), 7.83 d (1H, 3′-H, *E*, $^3J$ = 2.1 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 27.5 ($SCH_2$, *E*), 31.1 ($SCH_2$, *Z*), 106.1 q ($C^5$, *Z*, $^3J_{CF}$ = 2.2 Hz), 106.3 q ($C^5$, *E*, $^3J_{CF}$ = 2.2 Hz), 120.4 q ($CF_3$, $^1J_{CF}$ = 257.4 Hz), 121.3 (ClCH=, *Z*), 121.6 (ClCH=, *E*), 127.1 (=CH, *Z*), 128.3 (=CH, *E*), 128.8 ($C^{4'}$, *Z*), 128.8 ($C^{4'}$, *E*), 129.3 ($C^{3'}$, *Z*), 129.3 ($C^{3'}$, *E*), 132.1 ($C^{5'}$, *Z*), 132.1 ($C^{5'}$, *E*), 140.8 ($C^{2'}$, *E*), 140.9 ($C^{2'}$, *Z*), 156.1 q ($C^6$, *E*, $^2J_{CF}$ = 36.2 Hz), 156.2 q ($C^6$, *Z*, $^2J_{CF}$ = 36.2 Hz), 161.2 ($C^4$, *Z*), 161.3 ($C^4$, *E*), 173.3 ($C^2$, *Z*), 172.6 ($C^2$, *E*). Mass spectrum: *m*/*z* 336 $[M]^+$. Found, %: C 42.95; H 2.28; N 8.11;

S 18.94. $C_{11}H_8ClF_3N_2S_2$. Calculated, %: C 42.80; H 2.39; N 8.32; S 19.04.

**2-(3-Chlorobut-2-en-1-ylsulfanyl)-4-(thiophen-2-yl)-6-(trifluoromethyl)pyrimidine (Vd)** was synthesized in a similar way from 1.50 g (0.007 mol) of **IId** and 1.66 g (0.007 mol) of **IIIb**. Yield 2.14 g (82%), mp 84–85°C. IR spectrum (KBr), ν, $cm^{-1}$: 3110–3046, 2983–2850 (C–H); 1660, 1590, 1529 (C=C); 1180, 1146, 1125 (C–F); 719 (C–Cl). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: *Z* isomer: 2.12 s (3H, $CH_3$), 3.95 d (2H, $CH_2S$, $^3J$ = 7.1 Hz), 5.83 t (2H, =CH, $^3J$ = 7.1 Hz), 7.17 d.d (1H, 4′-H, $^3J$ = 4.8, 3.3 Hz), 7.45 s (1H, 5-H), 7.58 d (1H, 5′-H, $^3J$ = 4.8 Hz), 7.82 d (1H, 3′-H, $^3J$ = 3.3 Hz); *E* isomer: 2.18 s (3H, $CH_3$), 3.80 d (2H, $CH_2S$, $^3J$ = 7.1 Hz), 5.90 t (2H, =CH, $^3J$ = 7.1 Hz), 7.17 d.d (1H, 4′-H, $^3J$ = 4.8, 3.3 Hz), 7.45 s (1H, 5-H), 7.58 d (1H, 5′-H, $^3J$ = 4.8 Hz), 7.82 d (1H, 3′-H, $^3J$ = 3.3 Hz). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: *Z* isomer: 26.2 ($CH_3$), 29.6 ($CH_2S$), 106.1 q ($C^5$, $^3J_{CF}$ = 2.7 Hz), 120.5 q ($CF_3$, $^1J_{CF}$ = 275.7 Hz), 121.1 (=CH), 128.8 ($C^{4'}$), 129.3 ($C^{3'}$), 132.0 ($C^{5'}$), 134.1 (ClC=), 141.1 ($C^{2'}$), 156.23 q ($C^6$, $^2J_{CF}$ = 36.0 Hz), 161.23 ($C^4$), 173.71 ($C^2$). Mass spectrum: *m*/*z* 350 $[M]^+$. Found, %: C 44.67; H 2.79; N 7.98; S 18.46. $C_{13}H_{10}ClF_3N_2S_2$. Calculated, %: C 44.51; H 2.87; N 7.99; S 18.28.

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