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CYCLOCONDENSATION OF 2-AMINO-1,3,4-THIADIAZOLES WITH β-SULFONYLVINYL-TRIFLUOROMETHYLDIOLS

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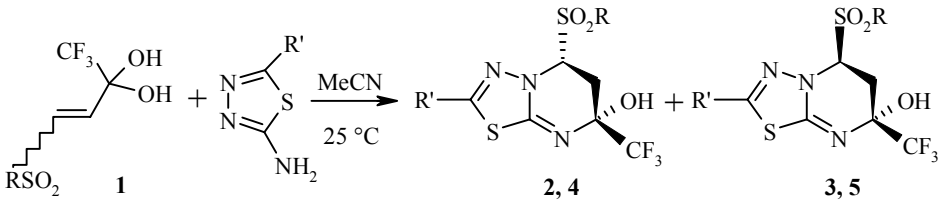
A series of CF_3-containing 6,7-dihydro-5H-[1,3,4]thiadiazolo[3,2-a]pyrimidin-7-ols was obtained by the interaction of 2-amino-1,3,4-thiadiazoles with β-sulfonylvinyltrifluoromethyldiols and their stereochemistry was established. The structure of 5-(phenylsulfonyl)-7-(trifluoromethyl)-6,7-dihydro-5H-[1,3,4]thiadiazolo[3,2-a]pyrimidin-7-ol was confirmed by X-ray crystallography.

Keywords: 2-amino-1,3,4-thiadiazoles, 6,7-dihydro-5H-[1,3,4]thiadiazolo[3,2-*a*]pyrimidines, β-sulfonylvinyltrifluoromethyldiols, cyclocondensation.

The heterocyclization of 2-amino-1,3,4-thiadiazoles with β-diketones, β-chlorovinyl ketones and aldehydes [1, 2], acetals of β-keto aldehydes and malonic aldehyde under acid conditions [3,4] has been described previously. The derivatives of 1,3,4-thiadiazolo[3,3-*a*]pyrimidine obtained gave methyne dyes [1,3] and had pesticidal, herbicidal, growth-regulating activity. However until now there are practically unknown methods for the synthesis of fluorine containing derivatives of 1,3,4-thiadiazolo[3,2-*a*]pyrimidines.

In this work the reaction of 2-amino-1,3,4-thiadiazoles with β-sulfonylvinyltrifluoromethyldiols **1a,b** was studied. The sulfones **1a,b** were obtained by oxidation of the corresponding readily available sulfides [6]. We have shown previously that the sulfones **1a,b** react readily with both C- [7] and N-nucleophiles [8] and also readily undergo cyclocondensation with such binucleophiles as 2-aminopyridines [9] and aminoazoles [10]. We have now extended this to the 2-amino-1,3,4-thiadiazoles.

6,7-Dihydro-5H-[1,3,4]thiadiazolo[3,2-*a*]pyrimidin-7-ols (**2-5**) are formed from the reaction of the sulfones **1a,b** with 2-amino-1,3,4-thiadiazoles in acetonitrile. The stability of the aminohydrin fragment of this class of compound arises from the electron-acceptor properties of the CF_3 groups [11]



1 a R = Ph, **b** R = Me; **1a** *E*/*Z* = 7/2; **1b** *E*

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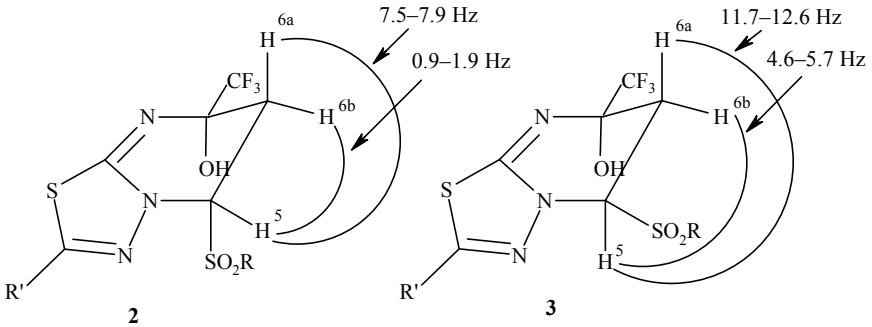
TABLE 1. Reaction of 2-Aminothiadiazoles with Sulfones **1a,b**

Compound	R	R'	mp,°C	**2/3** or **4/5**	Yield, %
2a / 3a	Ph	H	178	100 / 4	86
4a / 5a	Me	H	165	100 / <1	90
2b / 3b	Ph	Me	197	100 / 3	84
4b / 5b	Me	Me	186	100 / <1	88
2c / 3c	Ph	*t*-Bu	189	100 / 0	91
4c / 5c	Me	*t*-Bu	193	100 / 7	94
2d / 3d	Ph	4-$MeOC_6H_4$	208	100 / 1	94
4d / 5d	Me	4-$MeOC_6H_4$	199	100 / 17	91
2e / 3e	Ph	C_6H_5	181	100 / 9	92
4e/ 5e	Me	C_6H_5	176	100 / 32	90
2f / 3f	Ph	4-ClC_6H_4	202	100 / 10	81
4f / 5f	Me	4-ClC_6H_4	200	100 / 38	85
2g / 3g	Ph	2,4-$Cl_2C_6H_3$	214	100 / 10	88
4g / 5g	Me	2,4-$Cl_2C_6H_3$	208	100 / 40	90

Thiadiazoles with both alkyl and aryl substituents were used in the reaction. In either case isomeric cycloadducts **2-3, 4-5** were obtained in high yield. Note that all reactions occurred regiospecifically and stereoselectively. However when the thiadiazoles had strong electron-withdrawing substituents, e.g., a 4-nitrophenyl group, the reaction did not occur and we only succeeded in isolating starting materials.

^{1}H NMR spectroscopy was used to determine the stereochemistry of the cycloadducts . The position of the sulfonyl group in compounds **2-5** was estimated on the basis of the known values of the coupling constants for the ABX system of protons in the CH–CH_2 unit of the pyrimidine ring. For example in the ^{1}H NMR spectra of compounds **2,4** coupling was observed between the equatorial hydrogen 5-H and the hydrogens of the methylene group 6a-H and 6b-H with constants J = 0.9-1.9 and 7.5-7.9 Hz, while larger coupling constants (J = 11.7-12.6 Hz) were registered in the ^{1}H NMR spectra of compounds **3**, **5**. These values correspond to *axi-axi* interaction, which is only possible when hydrogen 5-H is in an axial position.



An X-ray structural study of 5-(phenylsulfonyl)-7-(trifluoromethyl)-6,7-dihydro-5H-[1,3,4]thiadiazolo-[3,2-*a*]pyrimidin-7-ol (**2a**) was carried out to confirm finally the structures of the cycloadducts **2-5**. It was revealed that the dihydropyrimidine ring in compound **2a** has an envelope conformation. It should be noted that the equatorial position of the trifluoromethyl group is favorable sterically because of its high conformational energy [1]. The unusual axial orientation of the phenylsulfonyl group is probably a result of the formation of an intramolecular hydrogen bond between the hydrogen atom of the hydroxy group and an oxygen atom of the sulfonyl group. A comparison of the chemical shifts of the CF_3 group in the ^{13}C NMR spectra of compound **2a** and the other cycloadducts **2-5** indicates the equatorial position of the trifluoromethyl groups in the latter.

TABLE 2. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %		NMR spectra (CD_3CN, CF_3COOH), δ, ppm (*J*, Hz)	
		C	H	^1H	^{13}C
1	2	3	4	5	6
2a	$C_{12}H_{10}F_3N_3O_3S_2$	39.31 / 39.45	2.59 / 2.76	2.90 (1H, dd, *J* = 7.5, 15.8, 6-H); 3.36 (1H, d, *J* = 15.8, 6-H); 6.05 (1H, d, *J* = 7.5, 5-H); 7.01 (1H, s, Ar); 7.71 (2H, t, Ar); 7.85 (1H, t, Ar); 7.93 (2H, d, Ar)	26.7, 73.6, 80.4 (q, *J* = 34.3, COH); 124.0 (q, *J* = 286.4, CF_3); 131.0, 131.4, 131.5, 137.6, 149.6, 169.5
3a				2.81 (1H, dd, *J* = 11.9, 14.2, 6-H); 3.08 (1H, dd, *J* = 5.7, 14.2, 6-H); 5.83 (1H, dd, *J* = 5.7, 11.9, 5-H); 6.73 (1H, s, Ar); 7.70 (2H, t, Ar); 7.85 (1H, t, Ar); 8.10 (2H, d, Ar)	
4a	$C_7H_8F_3N_3O_3S_2$	27.54 / 27.72	2.48 / 2.66	2.88 (1H, dd, *J* = 7.4, 15.9, 6-H); 3.20 (1H, d, *J* = 15.9, 6-H); 3.27 (3H, s, CH_3); 6.06 (1H, d, *J* = 7.4, 5-H); 7.19 (1H, s, Ar)	25.5, 42.3, 72.1, 80.3 (q, *J* = 35.5, COH); 124.0 (q, *J* = 286.7, CF_3); 150.1, 169.0
2b	$C_{13}H_{12}F_3N_3O_3S_2$	41.22 / 41.16	3.11 / 3.19	2.49 (3H, s, CH_3); 2.87 (1H, dd, *J* = 7.5, 15.9, 6-H); 3.36 (1H, d, *J* = 15.9, 6-H); 6.01 (1H, d, *J* = 7.5, 5-H); 7.69 (2H, t, Ar); 7.85 (1H, t, Ar); 7.92 (2H, d, Ar)	16.4, 26.6, 73.6, 80.3 (q, *J* = 34.1, COH); 124.0 (q, *J* = 287.0, CF_3); 131.3, 131.4, 131.7, 137.3, 158.2, 169.4
3b				2.49 (3H, s, CH_3); 2.74 (1H, d.d, *J* = 11.7, 14.5, 6-H); 3.05 (1H, dd, *J* = 5.7, 14.5, 6-H); 5.81 (1H, dd, *J* = 5.7, 11.7, 5-H); 7.69 (2H, t, Ar); 7.85 (1H, t, Ar); 8.08 (2H, d, Ar)	
4b	$C_8H_{10}F_3N_3O_3S_2$	30.16 / 30.28	3.13 / 3.18	2.68 (3H, s, CH_3); 2.86 (1H, dd, *J* = 7.5, 15.9, 6-H); 3.21 (1H, d, *J* = 15.9, 6-H); 3.26 (3H, s, CH_3); 6.03 (1H, d, *J* = 7.5, 5-H)	16.6, 25.6, 42.3, 72.0, 80.2 (q, *J* = 35.4, COH); 123.9 (q, *J* = 286.6, CF_3); 158.1, 169.2
2c	$C_{16}H_{18}F_3N_3O_3S_2$	45.51 / 45.60	4.22 / 4.30	1.23 (9H, s, $3CH_3$); 2.88 (1H, dd, *J* = 7.5, 15.7, 6-H); 3.40 (1H, d, *J* = 15.7, 6-H); 6.02 (1H, dd, *J* = 7.5, 0.9, 5-H); 7.69 (2H, t, Ar); 7.84 (1H, t, Ar); 7.93 (2H, d, Ar)	26.4, 29.5, 37.8, 73.3, 80.0 (q, *J* = 33.6, COH); 124.0 (q, *J* = 285.8, CF_3); 131.3, 131.4, 131.6, 137.5, 158.0, 172.8
4c	$C_{11}H_{16}F_3N_3O_3S_2$	36.64 / 36.76	4.40 / 4.49	1.45 (9H, s, $3CH_3$); 2.85 (1H, dd, *J* = 7.7, 15.9, 6-H); 3.20 (1H, d, *J* = 15.9, 6-H); 3.26 (3H, s, CH_3); 6.01 (1H, dd, *J* = 7.7, 1.5, 5-H)	26.6, 29.4, 38.9, 42.6, 72.0, 80.8 (q, *J* = 35.7, COH); 124.1 (q, *J* = 287.0, CF_3); 158.0, 169.8

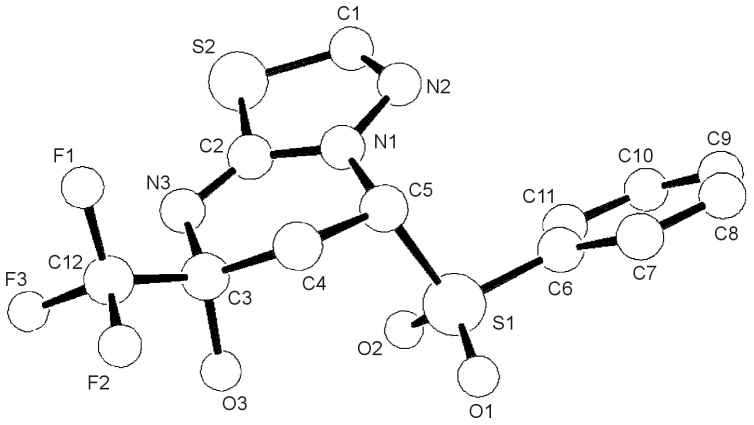
TABLE 2 (continued)

1	2	3	4	5	6
5c				1.45 (9H, s, $3CH_3$); 2.57 (1H, dd, *J* = 12.6, 13.9, 6-H); 2.94 (1H, dd, *J* = 4.9, 13.9, 6-H); 3.47 (3H, s, CH_3); 5.73 (1H, dd, *J* = 4.9, 12.6, 5-H)	
2d	$C_{19}H_{16}F_3N_3O_4S_2$	48.29 / 48.40	3.36 / 3.42	3.03 (1H, dd, *J* = 7.5, 15.6, 6-H); 3.46 (1H, d, *J* = 15.6, 6-H); 3.80 (3H, s, CH_3); 6.06 (1H, d, *J* = 7.5, 5-H); 6.94 (2H, d, Ar); 7.34 (2H, d, Ar); 7.62 (2H, t, Ar); 7.79 (1H, t, Ar); 7.89 (2H, d, Ar)	27.0, 58.8, 74.6, 81.1 (q, *J* = 35.3, COH); 117.0, 120.0, 124.4 (q, *J* = 285.0, CF_3); 126.7, 131.1, 131.7, 131.8, 138.0, 150.4, 166.6, 167.6
3d				2.82 (1H, br. t, *J* = 14.0, 6-H); 3.15 (1H, dd, *J* = 4.8, 14.0, 6-H); 3.80 (3H, s, CH_3); 5.81 (1H, dd, *J* = 4.8, 12.1, 5-H); 7.12 (2H, d, Ar); 7.38 (2H, d, Ar); 7.67 (2H, t, Ar); 8.06 (1H, t, Ar); 8.42 (2H, d, Ar)	
4d	$C_{14}H_{14}F_3N_3O_4S_2$	46.87 / 47.01	3.41 / 3.45	2.95 (1H, dd, *J* = 7.6, 15.6, 6-H); 3.28 (1H, d, *J* = 15.6, 6-H); 3.35 (3H, s, CH_3); 3.86 (3H, s, CH_3); 6.13 (1H, br. d, *J* = 7.6, 5-H); 7.07 (2H, d, Ar); 7.81 (2H, d, Ar)	24.7, 41.6, 55.5, 71.3, 79.3 (q, *J* = 35.3, COH); 115.7, 124.2 (q, *J* = 286.5, CF_3); 130.0, 131.9, 155.0, 166.0, 167.1
5d				2.66 (1H, br. t, *J* = 13.5, 6-H); 3.01 (1H, dd, *J* = 4.6, 13.5, 6-H); 3.58 (3H, s, CH_3); 3.87 (3H, s, CH_3); 5.86 (1H, dd, *J* = 4.6, 12.2, 5-H); 7.08 (2H, d, Ar); 7.78 (2H, d, Ar)	
2e	$C_{18}H_{14}F_3N_3O_3S_2$	48.85 / 48.97	3.16 / 3.20	3.03 (1H, dd, *J* = 7.5, 15.6, 6-H); 3.46 (1H, d, *J* = 15.6, 6-H); 3.80 (3H, s, CH_3); 6.06 (1H, d, *J* = 7.5, 5-H); 6.94 (2H, d, Ar); 7.34 (2H, d, Ar); 7.62 (2H, t, Ar); 7.79 (1H, t, Ar); 7.89 (2H, d, Ar)	26.9, 74.5, 81.0 (q, *J* = 35.4, COH); 124.2 (q, *J* = 286.1, CF_3); 127.8, 129.1, 131.6, 131.7, 131.8, 135.8, 138.0, 138.1, 158.0, 169.1
3e				2.82 (1H, br. t, *J* = 14.0, 6-H); 3.15 (1H, dd, *J* = 4.8, 14.0, 6-H); 3.80 (3H, s, CH_3); 5.81 (1H, dd, *J* = 4.8, 12.1, 5-H); 7.12 (2H, d, Ar); 7.38 (2H, d, Ar); 7.67 (2H, t, Ar); 8.06 (1H, t, Ar); 8.42 (2H, d, Ar)	
4e	$C_{12}H_{13}F_3N_3O_3S_2$	41.14 / 41.16	3.13 / 3.19	2.95 (1H, dd, *J* = 7.9, 15.8, 6-H); 3.28 (1H, dd, *J* = 1.3, 15.8, 6-H); 3.36 (3H, s, CH_3); 5.89 (1H, dd, *J* = 1.3, 7.9, 5-H); 7.59 (2H, t, Ar); 7.68 (1H, t, Ar); 7.86 (2H, d, Ar)	25.8, 42.7, 72.6, 80.5 (q, *J* = 35.2, COH); 124.1 (q, *J* = 286.4, CF_3); 129.2, 131.5, 131.6, 135.6, 161.4, 167.6
5e				2.65 (1H, br. t, *J* = 13.9, 6-H); 3.02 (1H, dd, *J* = 5.0, 13.9, 6-H); 3.58 (3H, s, CH_3); 5.89 (1H, dd, *J* = 5.0, 12.6, CH-5); 7.59 (2H, t, Ar); 7.68 (1H, t, Ar); 7.88 (2H, d, Ar)	26.2, 44.5, 71.4, 81.6 (q, *J* = 35.2, COH); 124.1 (q, *J* = 286.5, CF_3); 127.9, 130.8, 132.0, 135.6, 160.9, 168.7

TABLE 2 (continued)

1	2	3	4	5	6
2f	$C_{18}H_{13}ClF_3N_3O_3S_2$	45.28 / 45.43	2.69 / 2.75	2.99 (1H, dd, *J* = 7.6, 15.7, 6-H); 3.44 (1H, d, *J* = 15.7, 6-H); 6.11 (1H, dd, *J* = 1.2, 7.6, 5-H); 7.44 (2H, d, Ar); 7.52 (2H, d, Ar); 7.67 (2H, t, Ar); 7.85 (1H, t, Ar); 7.95 (2H, d, Ar)	26.7, 73.9, 80.6 (q, *J* = 35.4, COH); 124.2 (q, *J* = 286.2, CF_3); 125.8, 127.0, 129.9, 131.0, 131.1, 131.2, 131.7, 137.1, 156.9, 168.2
3f				2.84 (1H, dd, *J* = 12.4, 13.9, 6-H); 3.16 (1H, dd, *J* = 4.7, 13.9, 6-H); 5.96 (1H, dd, *J* = 4.7, 12.4, 5-H); 7.44 (2H, d, Ar); 7.52 (2H, d, Ar); 7.73 (2H, t, Ar); 7.85 (1H, t, Ar); 8.10 (2H, d, Ar)	
4f	$C_{13}H_{11}ClF_3N_3O_3S_2$	37.67 / 37.73	2.56 / 2.68	2.94 (1H, dd, *J* = 7.5, 15.6, 6-H); 3.27 (1H, br. d, *J* = 15.6, 6-H); 3.34 (3H, s, CH_3); 6.14 (1H, dd, *J* = 1.9, 7.5, 5-H); 7.60 (2H, d, Ar); 7.87 (2H, d, Ar)	25.8, 42.5, 72.2, 80.1 (q, *J* = 35.5, COH); 124.3 (q, *J* = 286.1, CF_3); 130.2, 131.1, 131.6, 140.9, 149.4, 166.7
5f				2.66 (1H, dd, *J* = 12.5, 14.0, 6-H); 3.01 (1H, dd, *J* = 4.6, 14.0, 6-H); 3.56 (3H, s, CH_3); 5.86 (1H, dd, *J* = 4.6, 12.5, 5-H); 7.60 (2H, d, Ar); 7.85 (2H, d, Ar)	
2g	$C_{18}H_{12}Cl_2F_3N_3O_3S_2$	42.29 / 42.36	2.33 / 2.37	3.01 (1H, dd, *J* = 7.6, 15.8, 6-H); 3.47 (1H, d, *J* = 15.8, 6-H); 6.14 (1H, br. d, *J* = 7.6, 5-H); 7.28 (1H, d, Ar); 7.36 (1H, d, Ar); 7.60 (1H, s, Ar); 7.65 (2H, t, Ar); 7.80 (1H, t, Ar); 7.91 (2H, d, Ar)	27.6, 72.6, 81.6 (q, *J* = 35.4, COH); 124.4 (q, *J* = 286.6, CF_3); 128.0, 130.5, 131.8, 131.9, 132.0, 133.0, 133.4, 134.4, 135.6, 137.1, 156.9, 167.7
3g				2.83 (1H, dd, *J* = 12.5, 13.6, 6-H); 3.16 (1H, dd, *J* = 5.0, 13.6, 6-H); 5.96 (1H, dd, *J* = 5.0, 12.5, 5-H); 7.32 (1H, d, Ar); 7.40 (1H, d, Ar); 7.57 (1H, s, Ar); 7.65 (2H, t, Ar); 7.80 (1H, t, Ar); 8.04 (2H, d, Ar)	
4g	$C_{13}H_{10}Cl_2F_3N_3O_3S_2$	34.73 / 34.83	2.27 / 2.25	2.95 (1H, dd, *J* = 7.6, 15.8, 6-H); 3.30 (1H, br. d, *J* = 15.8, 6-H); 3.33 (3H, s, CH_3); 6.18 (1H, br. d, *J* = 7.6, 5-H); 7.50 (1H, d, Ar); 7.65 (1H, s, Ar); 8.02 (1H, d, Ar)	25.7, 42.4, 72.5, 80.2 (q, *J* = 35.3, COH); 124.0 (q, *J* = 286.5, CF_3); 125.8, 130.3, 132.4, 132.9, 133.6, 141.6, 156.9, 167.5
5g				2.66 (1H, br. t, *J* = 13.9, 6-H); 3.01 (1H, dd, *J* = 4.7, 13.9, 6-H); 3.53 (3H, s, CH_3); 5.87 (1H, dd, *J* = 4.7, 12.5, 5-H); 7.50 (1H, d, Ar); 7.65 (1H, s, Ar); 7.92 (1H, d, Ar)	

* IR spectra, cm^{-1}: 1100-1300 (CF_3), 1370-1385 (SO_2), 3100-3400 (OH).



General view of molecule **2a** with atom numbering.

It is interesting that in the case of the compounds with the methylsulfonyl groups the proportion of the isomers **3** and **5** with the sulfonyl group in the equatorial position is greater than in the case of the phenylsulfonyl substituted cycloadducts. This is probably explained by the more stable hydrogen bond in compounds **2** and **4**. In addition a greater proportion of the of the isomers **3** and **5** was observed in mixtures of the stereoisomers of compounds **2, 3, 4,** and **5** with increasing electron-accepting ability of the aryl substituents in the starting thiadiazole.

TABLE 3. Basic Bond Lengths *d* and Bond Angles ω in Compound **2a**

Bond	*d*, Δ	Angle	ω, deg.
S(1)–O(1)	1.424(3)	O(1)–S(1)–O(2)	120.8(2)
S(1)–O(2)	1.426(3)	O(1)–S(1)–C(6)	108.44(18)
S(1)–C(6)	1.748(3)	O(2)–S(1)–C(6)	107.8(2)
S(1)–C(5)	1.830(3)	O(1)–S(1)–C(5)	105.31(18)
S(2)–C(1)	1.729(4)	O(2)–S(1)–C(5)	108.54(17)
S(2)–C(2)	1.748(3)	C(6)–S(1)–C(5)	104.88(14)
F(1)–C(12)	1.335(4)	C(1)–S(2)–C(2)	89.00(16)
F(2)–C(12)	1.330(4)	C(2)–N(1)–N(2)	117.9(2)
F(3)–C(12)	1.334(4)	C(2)–N(1)–C(5)	121.7(2)
O(3)–C(3)	1.403(4)	N(2)–N(1)–C(5)	120.3(2)
N(1)–C(2)	1.367(4)	C(1)–N(2)–N(1)	109.2(3)
N(1)–N(2)	1.380(4)	C(2)–N(3)–C(3)	116.5(2)
N(1)–C(5)	1.427(4)	N(2)–C(1)–S(2)	116.8(3)
N(2)–C(1)	1.270(4)	N(3)–C(2)–N(1)	128.5(3)
N(3)–C(2)	1.282(4)	N(3)–C(2)–S(2)	124.4(2)
N(3)–C(3)	1.456(4)	N(1)–C(2)–S(2)	107.1(2)
C(3)–C(12)	1.523(5)	O(3)–C(3)–N(3)	110.9(2)
C(3)–C(4)	1.529(4)	O(3)–C(3)–C(12)	107.3(2)
C(4)–C(5)	1.522(5)	N(3)–C(3)–C(12)	106.4(3)
C(6)–C(11)	1.364(6)	O(3)–C(3)–C(4)	108.9(3)
C(6)–C(7)	1.383(5)	N(3)–C(3)–C(4)	114.7(3)
C(7)–C(8)	1.367(7)	C(12)–C(3)–C(4)	108.4(3)
C(8)–C(9)	1.366(9)	C(5)–C(4)–C(3)	113.9(3)
C(9)–C(10)	1.351(9)	N(1)–C(5)–C(4)	108.8(2)
C(10)–C(11)	1.395(8)	N(1)–C(5)–S(1)	110.6(2)
		C(4)–C(5)–S(1)	113.8(2)
		C(11)–C(6)–C(7)	121.5(4)
		C(11)–C(6)–S(1)	119.0(3)
		C(7)–C(6)–S(1)	119.4(3)

In conclusion, interaction of 2-amino-1,2,4-thiadiazoles with β-sulfonylvinyltrifluoromethyldiols **1a,b** in acetonitrile leads to the regiospecific and stereoselective formation of CF_3-containing 6,7-dihydro-5H-[1,3,4]thiadiazolo[3,2-*a*]pyrimidin-7-ols. The undoubted value of the synthesis is the simplicity of the reaction and the ease of separation and practically quantitative yields of the valuable reaction products.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR-400 spectrometer (working frequencies 400 and 100 MHz respectively) in CD_3CN/TFA (95/5) with TMS as internal standard. IR spectra of nujol mulls were recorded with UR-20 spectrometer. TLC analysis was carried out on Silufol UV-254 plates developed with acidified $KMnO_4$ and iodine vapor.

X-ray Structural Investigation of a Single Crystal of Compound 2a with dimensions 0.62 × 0.48 × 0.31 mm was carried at room temperature on an Enraf-Nonius CAD-4 diffractometer (MoKα radiation, θ/2θ scanning, range θ = 2.15 to 24.95°, $0 \le h \le 8$, $0 \le k \le 26$, $-22 \le l \le 22$. Of the 1870 reflexions collected, 1736 were symmetrically independent (*R* factor average 0.0238). Crystals of compound **2a** are monoclinic, $a = 8.160(2)$, $b = 22.729(5)$, $c = 18.945(4)$ Å; $\beta = 90.56(3)$; $V = 3513.5(14)$ Å^3. M = 365.35; $Z = 8$; $d_{calc} = 1.382$ g/cm^3, space group *C*2/*c*. The structure was solved by direct method and refined by full matrix least squares method (1736 reflexions with $I > 2\sigma$, 253 parameters) to a final $R = 0.0037$, $R_w = 0.103$. Hydrogen atoms in the isotropic approximation were revealed in the difference synthesis of the electron density. Structural data have been deposited in the Cambridge Crystallographic Data Bank (entry no. CCDC 161489).

General Method for the Synthesis of the Heterocyclic Compounds 2-5. To a solution of sulfone **1a,b** (1 mmol) in acetonitrile (5 ml) was added at room temperature a solution of the corresponding 2-amino-1,2,4-thiadiazole (1 mmol) dissolved in the minimum amount of acetonitrile. The course of the reaction was monitored by TLC. The 6,7-dihydro-5H-[1,3,4]thiadiazolo[3,2-*a*]pyrimidin-7-ols **2-5** produced were filtered off and washed with acetonitrile (3 × 1 ml).

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