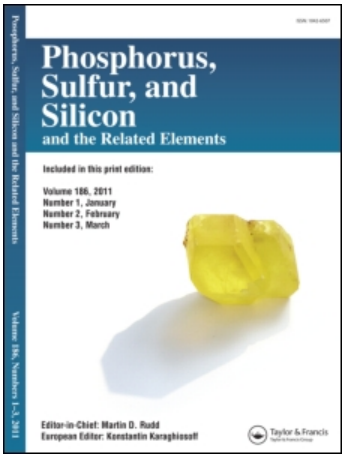

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Marion Kleist[a]; Pedro Chume[a]; Helmut Reinke[a]; Joachim Teller[a]; Heinz Dehne[a]
[a] Department of Chemistry, University of Rostock, Rostock, Germany

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DERIVATIVES OF *trans* 5-AROYL-3,4-DIARYLTHIAZOLIDINE-2-IMINES

MARION KLEIST*, PEDRO CHUME, HELMUT REINKE, JOACHIM TELLER and HEINZ DEHNE

University of Rostock, Department of Chemistry, Buchbinderstr. 9, D-18051 Rostock, Germany

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The synthesis of *trans* 5-aroyl-3,4-diarylthiazolidine-2-iminium chlorides **2** or *trans* 2-aroyl-1-aryl-1,2-dihydro-thiazolo[3,2-a]quinazoline-5-ones **3** by treatment of *threo* 1,3-diaryl-3-arylamino-2-thiocyanatopropanones **1** with dry hydrogen chloride is described. The reaction of the salts **2** with several acid chlorides yields the corresponding 2-(aroylimino), 2-(arylsulfenylimino) and 2-(arylsulfonylimino) substituted thiazolidines **6**, **7** and **8**, respectively.

Keywords: Threo 1,3-diaryl-3-arylamino-2-thiocyanatopropanones; *trans* 2-aroyl-1-aryl-1,2-dihydro-thiazolo[3,2-a]quinazoline-5-ones; 2-(aroylimino)thiazolidines; 2-(aryl-sulfenylimino)thiazolidines; 2-(arylsulfonylimino)thiazolidines; X-ray analysis

INTRODUCTION

Recently we reported the syntheses of arylsulfenyl, arylsulfinyl and corresponding sulfonyl derivatives of 4-thiazoline-2-imines by several acylation or oxidation steps.[1,2] In order to obtain other similar imino substituted heterocycles we investigated analogous acylations of thiazolidine-2-iminium chlorides **2** which are available by cyclization of β-amino α-thiocyanato ketones **1**.

* Corresponding Author.

RESULTS AND DISCUSSION

1,3-Diaryl-3-arylamino-2-thiocyanatopropanones **1** were prepared by aminomethylation of α-thiocyanatoacetophenones, aromatic aldehydes and arylamines (see Experimental, Table IV).[3] An increase of the yield was observed in some cases by treatment of the phenacyl thiocyanates with the corresponding *N*-benzylideneanilines.[4] After purification of the compounds **1** by recrystallization from acetone the racemate of only one diastereomer identified as *threo* was isolated. In the ^{1}H NMR spectra determined in DMSO-d_6 solution the coupling constant $^3J_{23}$ between the protons at the adjacent asymmetric centres is observed to be about 10 Hz. In addition, in the IR spectra the characteristic bands of the amino and thiocyanato group appear in the 3305 – 3409 cm^{-1} and 2155 – 2163 cm^{-1} region, comparable with that being recorded in [5–7]. These spectroscopic data (see Experimental, Table VI) correspond with the *threo* configuration in the favoured *anti-periplanar* conformation with regard to the hydrogen atoms as shown in Figure 1.

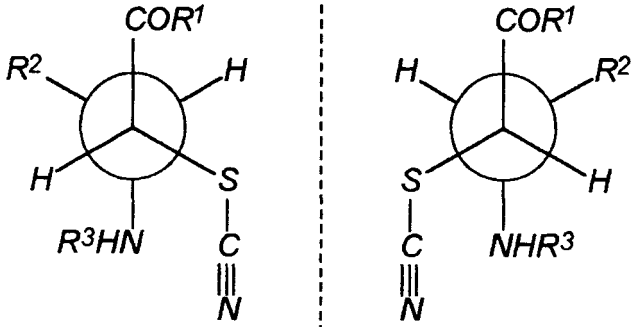
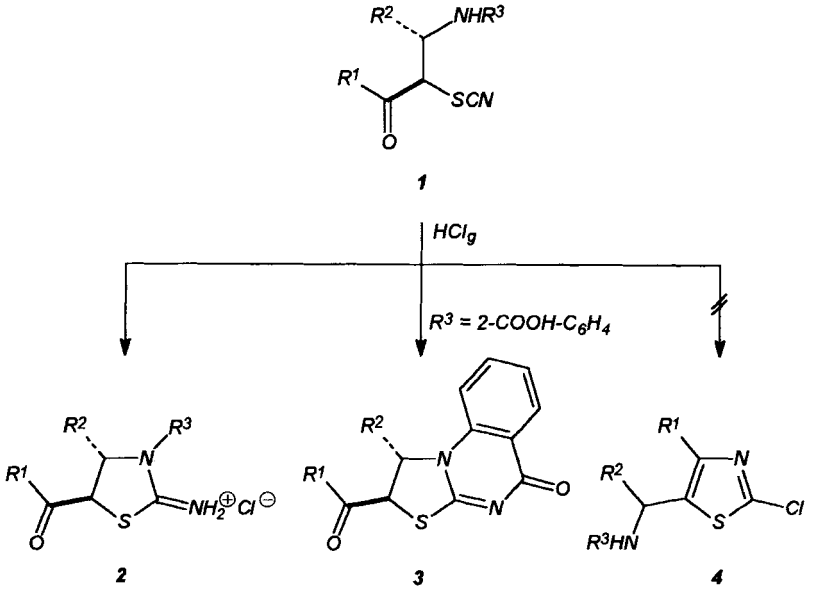


FIGURE 1 Pair of antipodes of the *threo* 1,3-diaryl-3-arylamino-2-thiocyanatopropanone **1**

This convenient vicinal arrangement of the amino and thiocyanato group in the acyclic compounds **1** should render possible an intramolecular cyclization, similar to those refered in other reactions [8–19]. In many cases such a nucleophilic addition proceeds already during attempts to synthesize compounds of that type and gives imino or amino substituted nitrogen and sulfur-containing heterocycles. The ring closure proceeds successfully both via acid and base catalysis.

We treated the *threo* 1,3-diaryl-3-arylamino-2-thiocyanatopropanones **1** suspended in chloroform with dry hydrogen chloride. In this way the corresponding thiazolidine-2-iminium chlorides **2**are obtained from **1a** – **1f** [20] and the 1,2-dihydrothiazolo[3,2-a]quinazoline-5-ones **3** from the carboxy-substituted compounds **1g** – **1k** (see Experimental, Table V). A formation of 2-chlorothiazoles **4** as described for reactions of α-thiocyanato ketones with hydrogen chloride [21–26] is not observed (Scheme 1).

The compounds **2** and **3** should keep the configuration of the acyclic precursors **1** at the asymmetric centres and, accordingly, are isolated as racemate of the *trans* isomers.

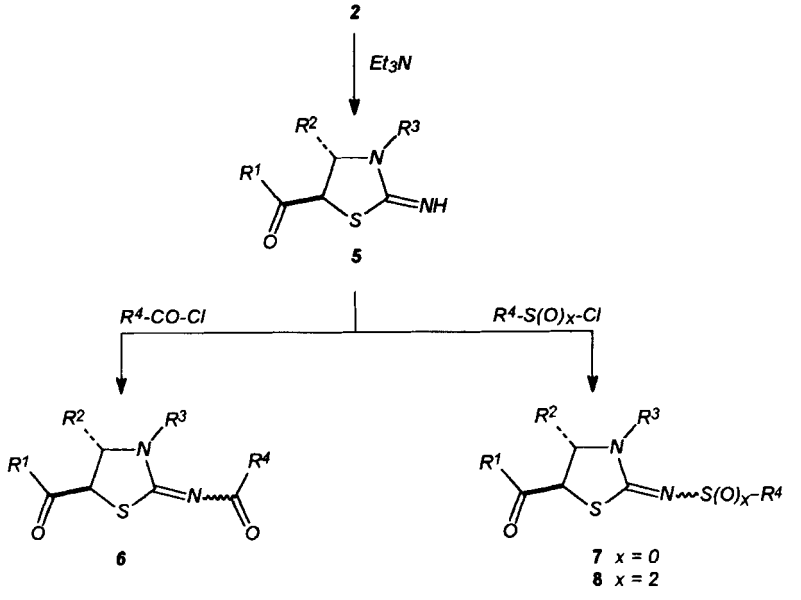


SCHEME 1

Iminium chlorides **2** were converted into the respective *trans* 5-aroyl-3,4-diarylthiazolidine-2-imines **5** by treatment of the salts **2** with weak bases like triethylamine or potassium hydrogen carbonate.[20] Heterocycles **5** are difficult to obtain in a well-crystalline form and are not fully purified. Therefore, compounds **5** were not isolated, but were characterized as their 2-(*N*-substituted imino)thiazolidines **6** (Table VII), **7** (Table

VIII) and **8** (Table IX) by reaction of **2** with the corresponding acid chlorides in the presence of triethylamine. However, 2-(arylsulfinylimino)thiazolidines could not be obtained by this way (Scheme 2).

In addition, we have observed that 2-(arylsulfenylimino), 2-(arylsulfinylimino) and 2-(arylsulfonylimino) substituted 4-thiazolines [1], 5-halo-4-thiazolines [2] and the corresponding thiazolidines **6**, **7** and **8**, respectively, occur preferentially as Z diastereomer in the solid state.



SCHEME 2

The data of mass, IR, ^{1}H NMR and ^{13}C NMR spectra (Table VI and X) prove the expected structures of the products **3, 6, 7** and **8**, respectively (for **1** see also Table IV).

In the infrared spectra we are especially interested in the position of C=O bands. The carbonyl frequency of the keto group in heterocyclic ring position **5** is found in all corresponding derivatives at about 1680 cm^{-1}. However, the CO vibration band of the imide group in the *N*-acylated compounds **3** and **6** is observed at distinct lower wavenumbers located at about 1640 cm^{-1} for **3** and at the 1625 cm^{-1} region for **6**. In the ^{13}C NMR spectra of the thiazolidine derivatives **6** these different C=O peaks can be found about 193 and 175 ppm.

In the ^{1}H NMR spectra of the derivatives of *trans* 5-aroyl-3,4-diarylthiazolidine-2-imines **3, 6, 7** and **8** the two methine ring protons are observed as two sets of doublets. The corresponding coupling constants vary from 1.2 to 3.0 Hz, depending on the imino substituent and the solvent used.

In addition, described structures are confirmed by X-ray crystal structure analysis of *trans* 2-benzoyl-1,2-dihydro-1-phenyl-thiazolo[3,2-a]quinazoline-5-one **3a** (Fig. 2), *trans* 5-benzoyl-2-(4-methylbenzoylimino)-3-(4-methylphenyl)-4-phenylthiazolidine **6c** (Fig. 3), *trans* 5-benzoyl-3-(4-chlorophenyl)-2-(4-chlorophenylsulfenylimino)-4-phenylthiazolidine **7e** (Fig. 4) and *trans* 5-benzoyl-4-(4-methylphenyl)-2-(4-methylphenylsulfonylimino)-3-phenylthiazolidine **8e** (Fig. 5). The figures 2 – 5 show only one enantiomer of the racemates.

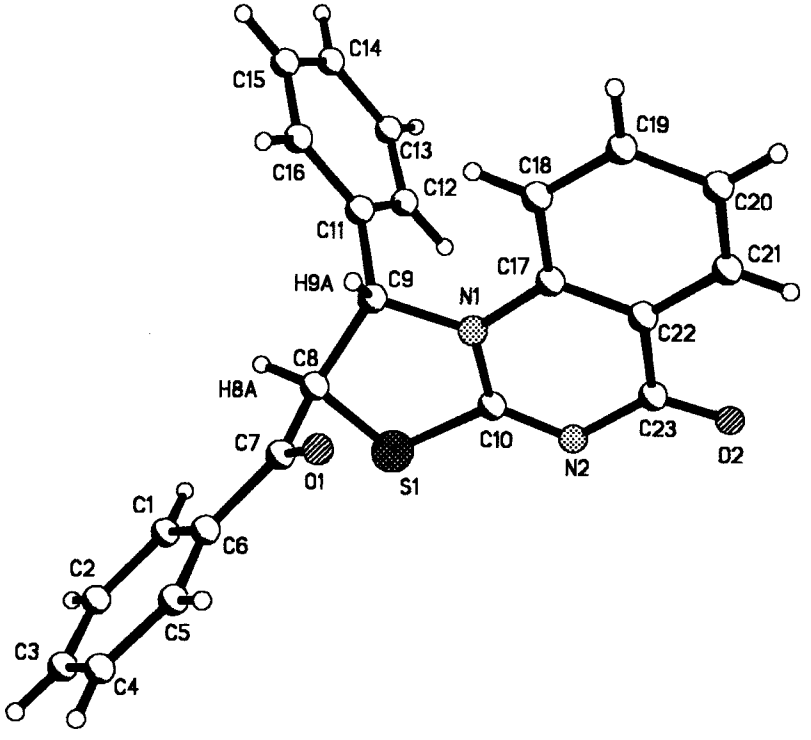


FIGURE 2 Molecular structure of *trans* 2-benzoyl-1 ,2-dihydro-1-phenyl-thiazolo[3,2-a]quinazoline-5-one **3a**

It must be mentioned that the compound **3a** crystalized with ethanol. The solvent molecule appears in different disordered positions near the centre of inversion. Consequently, the residual electron density could be used only to refine the position of the disordered nonhydrogen solvent atoms

TABLE I Selected bond distances [pm]

	3a	*6c*	*6c'*	*7e*	*8e*
O1-C7	122.0 (4)	120.4 (6)	121.3 (6)	122.3 (6)	121.2 (3)
C8-C9	153.8 (4)	155.1(6)	153.5 (7)	152.7 (7)	153.0 (4)
N1-C9	147.4 (4)	147.4 (6)	148.3 (6)	146.2 (6)	147.2 (3)
N1-C10	135.3 (4)	135.2 (6)	133.7 (6)	137.5 (6)	134.7 (3)
S1-C10	175.1(3)	176.0 (5)	176.2 (5)	177.3 (5)	177.7 (3)
S1-C8	182.1 (3)	181.4 (5)	184.4 (5)	183.9 (5)	182.4 (3)
N2-C10	130.1(4)	129.3 (6)	130.4 (6)	128.7 (6)	130.3 (3)
N2-C23	138.7 (4)	-	-	-	-
N2-C24	-	137.5 (6)	138.2 (6)	-	-
O2-C23	122.4 (4)	-	-	-	-
O2-C24	-	123.6 (6)	122.6 (6)	-	-
N2-S2	-	-	-	169.1 (5)	162.1 (2)
S2-O2	-	-	-	-	143.1(2)
S2-O3	-	-	-	-	143.9 (2)
C8-H8A	98.0	98.0	98.0	98.0	99.0
C9-H9A	98.0	98.0	98.0	98.0	99.0

The crystal structures of the *N*-acylated compounds **3a** and **6c** are comparable with those of sulfenyl and sulfonylimino derivatives **7e** and **8e** with regard to the observed bond lengths and angles of the thiazolidine ring (Table I and II). The bond distances between the N1 and C10 atoms are much shorter than the distance N1-C9 but longer than the length of the N2-C10 bond. This means that the N1-C10 bond has partial double-bond character (standard values: C=N 127 pm; C-N 147 pm) which is in agreement with the corresponding IR and NMR spectra.

Besides, we have studied the conformation of such *trans* substituted thiazolidines. In this connection the occurrence of two different twisted ring rotamers in the asymmetric unit of the unit cell of the 2-aroylimino derivative **6c** is remarkable. In one molecule the central heterocyclic ring is nearly planar, while the other has similar torsion angles like the heterocycles **3a**, **7e** and **8e**. This twisted five-membered ring appears to be favoured in solids as well as in solution. The torsional angle H8A-C8-C9-H9A in the solid state agrees with those determined by coupling constants of the respective proton NMR study (see Table VI and X).

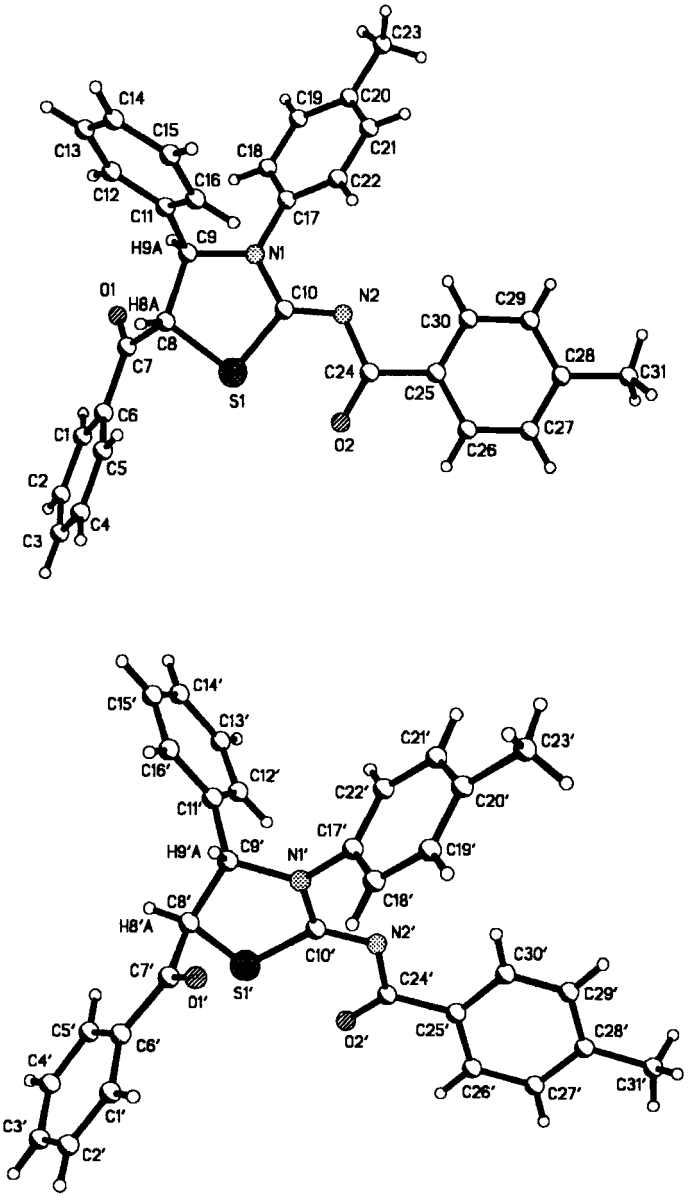


FIGURE 3 Molecular structures of *trans* 5-benzoyl-2-(4-methylbenzoylimino)-3-(4-methylphenyl)-4-phenylthiazolidine **6c**

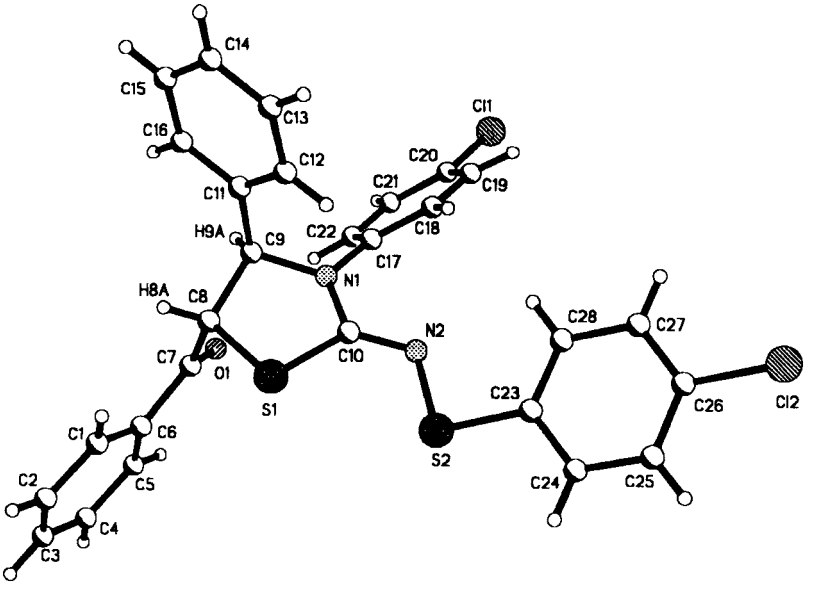


FIGURE 4 Molecular structure of *trans* 5-benzoyl-3-(4-chlorophenyl)-2-(4-chlorophenyl-sulfenylimino)-4-phenyl-thiazolidine **7e**

TABLE II Selected bond and torsional angles [°]

	3a	*6c*	*6c'*	*7e*	*8c*
C8-S1-C10	91.5 (2)	93.1(2)	91.0 (2)	91.6 (2)	90.5 (1)
N2-S2-C23	-	-	-	99.6 (2)	-
N2-S2-C24	-	-	-	-	104.9 (1)
O2-S2-O3	-	-	-	-	117.7 (1)
C10-N2-C23	117.3(3)	-	-	-	-
C10-N2-C24	-	118.4(4)	118.2(4)	-	-
C10-N2-S2	-	-	-	116.7 (4)	120.3 (2)
H8A-C8-C9-H9A	+96.2 (1)	-121.8 (1)	+96.5 (1)	-92.2 (1)	+90.1 (1)
S1-C8-C9-N1	+28.1 (3)	+2.7 (5)	-27.0 (5)	+34.4 (4)	-35.3 (2)
C7-C8-C9-C11	+148.4 (3)	+119.7 (5)	-148.4 (5)	+150.8 (4)	-154.6 (2)
C8-C9-N1-C10	-22.1 (3)	+1.3(6)	-22.8 (6)	+32.1 (5)	-26.9 (3)
C9-N1-C10-S1	-5.0 (3)	-0.8 (6)	-6.8 (6)	+13.4 (5)	-4.5 (3)
N1-C10-S1-C8	+11.3 (2)	-2.1 (4)	+9.3 (4)	-7.7 (4)	+15.6 (2)
C10-S1-C8-C9	+23.0 (2)	-2.7 (4)	+21.3 (4)	-24.7 (3)	+29.7 (2)

	3a	*6c*	*6c'*	*7e*	*8c*
S1-C10-N2-C23	-176.7 (2)	-	-	-	-
S1-C10-N2-C24	-	0.0 (7)	+2.6 (7)	-	-
S1-C10-N2-S2	-	-	-	-5.5 (6)	+3.9 (3)

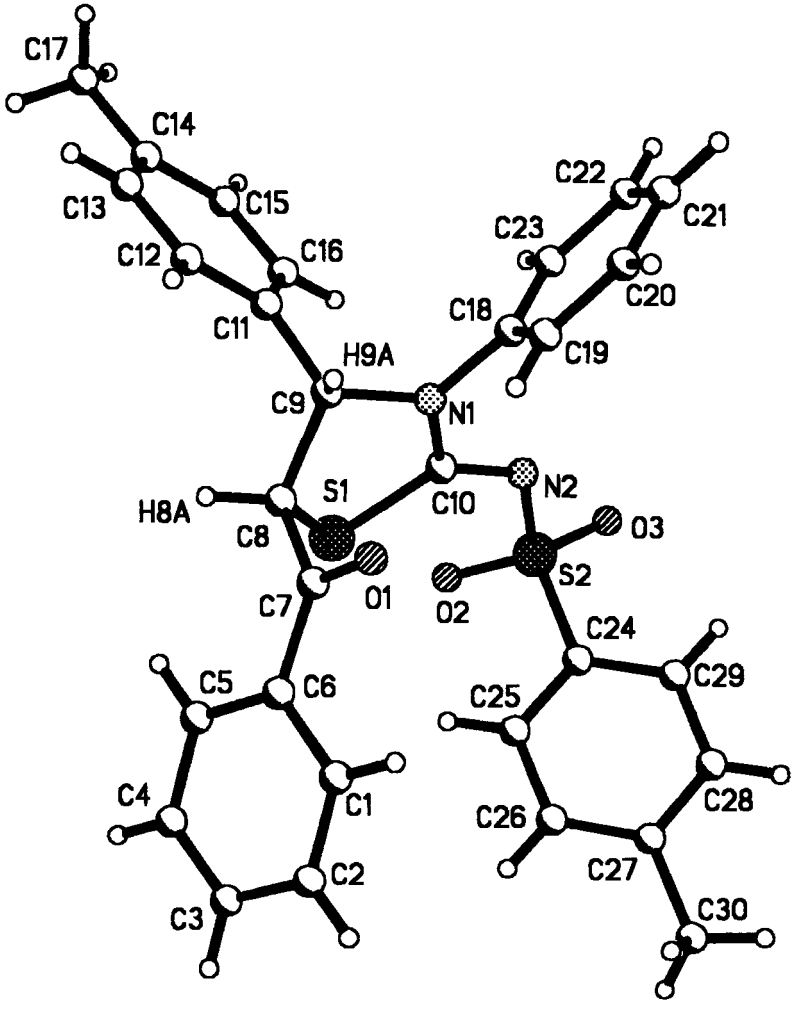


FIGURE 5 Molecular structure of *trans* 5-benzoyl-4-(4-methylphenyl)-2-(4-methylphenylsulfonylimino)-3-phenylthiazolidine **8e**

TABLE III Crystal and structure solution data for compounds **3a**, **6c**, **7e** and **8e**

	3a	*6c*	*7e*	*8e*
Formula	$C_{23}H_{16}N_2O_2S.C_2H_5OH$	$C_{31}H_{26}N_2O_2S$	$C_{28}H_{20}Cl_2N_2OS_2$	$C_{30}H_{26}N_2O_3S_2$
M [g mol^{-1}]	430.51	490.60	535.48	526.65
a [Å]	10.422(2)	12.861(3)	9.315(2)	10.599(1)
b [Å]	13.057(3)	29.125(1)	11.548(3)	17.404(1)
c [Å]	15.633(3)	15.273(3)	14.262(4)	14.604(1)
α [°]	90	90	111.74(2)	90
β [°]	90.54(3)	113.77(1)	91.40(1)	98.03(1)
γ [°]	90	90	111.83(2)	90
V [$Å^3$]	2127.2(8)	5235.6(24)	1299.2(6)	2667.5(3)
ρ calcd. [g cm^{-1}]	1.344	1.245	1.369	1.311
Z	4	8	2	4
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group (No. I.T.)	$P2_1/n$ (14)	$P2_1/c$ (14)	P_1 (2)	$P2_1/n$ (14)
F(000) e	904	2064	552	1104
μ (Mo- K_α) [mm^{-1}]	0.182	0.154	0.435	0.234
Crystal size [mm]	0.4 × 0.6 × 0.15	0.8 × 0.6 × 0.42	0.5 × 0.4 × 0.22	0.94 × 0.68 × 0.52
Temperature [°C]	20	20	25	-60
Scan range (2Θ) [°]	4.06/45	3.74/44	4.06/45	3.66/44
hkl range	-11/1–14/1, –17/17	-7/14, –29/32, –16/15	0/10, –11/10, –15/15	-9/11, –1/19, –16/16
Measured refl.	3666	7832	3547	4231
Unique refl.	2778	6428	3308	3275
Observed refl.	2098	3613	2170	2805

	3a	*6c*	*7e*	*8e*
Refined param.	285	649	318	351
R1 for observed	0.0499	0.0652	0.0625	0.0415
R1 for all	0.0717	0.1351	0.0987	0.0496
wR2 for all	0.1445	0.1796	0.1753	0.1135
GoF	1.043	1.024	1.021	1.016
$\Delta\rho$ (max/min) [e/ Å^3]	0.235/-0.186	0.220/-0.239	0.653/-0.265	0.280/-0.278

TABLE IV Analytical data of *threo* 1,3-diaryl-3-arylamino-2-thiocyanatopropanones **1**

1	R^1	R^2	R^3	*Yield (%)*	*Mp. (°C)*	*Empirical formula Molecular mass/ MS found*	*Analysis calculated/found (%)*			
							C	*H*	*N*	*S*
a	C_6H_5	C_6H_5	C_6H_5	78	139–141	$C_{22}H_{18}N_2OS$	73.72	5.06	7.81	8.94
						358.46 / 358	73.98	4.67	7.66	9.11
b	C_6H_5	C_6H_5	4-CH_3-C_6H_4	68	122–125	$C_{23}H_{20}N_2OS$	74.16	5.41	7.52	8.61
						372.48/372	74.02	5.12	7.58	8.82
c	C_6H_5	C_6H_5	3-Cl-C_6H_4	48	143–145	$C_{22}H_{17}ClN_2OS$	67.25	4.36	7.13	8.16
						392.90/392	66.99	4.21	7.18	8.38
d	C_6H_5	C_6H_5	4-Cl-C_6H_4	70	133–135	$C_{22}H_{17}ClN_2OS$	67.25	4.36	7.13	8.16
						392.90/392	67.46	4.44	7.02	8.16
e	C_6H_5	4-CH_3-C_6H_4	C_6H_5	65	138–140	$C_{23}H_{20}N_2OS$	74.16	5.41	7.52	8.61
						372.48 /372	74.43	5.38	7.33	8.52
f	C_6H_5	4-Cl-C_6H_4	C_6H_5	69	141–143	$C_{22}H_{17}ClN_2OS$	67.25	4.36	7.13	8.16
						392.90/392	67.03	4.21	7.23	8.25
g	C_6H_5	C_6H_5	2-COOH-C_6H_4	30	129–131	$C_{23}H_{18}N_2O_3S$	68.64	4.51	6.96	7.96
						402.47/402	68.57	4.46	6.84	7.85
h	C_6H_5	3-CH_3-C_6H_4	2-COOH-C_6H_4	29	118–120	$C_{24}H_{20}N_2O_3S$	69.21	4.84	6.73	7.70
						416.49/416	69.45	4.80	6.92	7.65
i	C_6H_5	4-CH_3-C_6H_4	2-COOH-C_6H_4	32	120–122	$C_{24}H_{20}N_2O_3S$	69.21	4.84	6.73	7.70
						416.49/416	69.41	4.60	6.79	7.84
j	C_6H_5	4-$(CH_3)_2CH$-C_6H_4	2-COOH-C_6H_4	20	112–113	$C_{26}H_{24}N_2O_3S$	70.25	5.44	6.30	7.21
						444.55/444	70.12	5.38	6.48	7.08
k	C_6H_5	2-thienyl	2-COOH-C_6H_4	31	106–108	$C_{21}H_{16}N_2O_3S_2$	61.75	3.95	6.86	15.70
						408.49/408	61.65	3.99	6.72	15.53

TABLE V Analytical data of *trans* 2-aroyl-1-aryl-1,2-dihydro-thiazolo[3,2-a]quinazoline-5-ones **3**

3	R^1	R^2	*Yield (%)*	*Mp. (°C)*	*Empirical formula Molecular mass/ MS found*	*Analysis calcumted/found (%)*			
						C	*H*	*N*	*S*
a	C_6H_5	C_6H_5	80	159–161	$C_{23}H_{16}N_2O_2S$	71.86	4.19	7.29	8.34
					384.45/384	71.90	4.37	7.43	8.43
b	C_6H_5	3-CH_3-C_6H_4	85	162–164	$C_{24}H_{16}N_2O_2S$	72.34	4.55	7.03	8.05
					398.48/398	72.02	4.46	7.12	8.09
c	C_6H_5	4-CH_3-C_6H_4	86	159–161	$C_{24}H_{16}N_2O_2S$	72.34	4.55	7.03	8.05
					398.48/398	72.13	4.37	7.13	7.97
d	C_6H_5	4-$(CH_3)_2$CH-C_6H_4	70	133–135	$C_{28}H_{22}N_2O_2S$	73.21	5.20	6.57	7.52
					426.53 /426	73.47	5.28	6.26	7.28
e	C_6H_5	2-thienyl	61	142–145	$C_{21}H_{14}N_2O_2S_2$	64.60	3.61	7.17	16.42
					390.47/390	64.52	3.75	7.05	16.57

TABLE VI Spectroscopic data of the compounds **1** and **3**

	IR spectra (KBr) ($\tilde{\nu}$ in cm^{-1})			*^{1}H NMR data ([a] DMSO-d6 ; [b] $CDCl_3$) (δ in ppm)*
	$\nu_{C=O}$	ν_{SCN}	ν_{NH}	
1a	1672	2155	3409	[a] 5.02 (t, 1H, C-3); 5.77 (d, 1H, C-2); 6.33 (d, 1H, NH); 6.53–7.80 (m, 15H, arom.H); $^3J_{23}$= 10.1 Hz; $^3J_{3N}$ = 10.4 Hz
1b	1671	2157	3408	[a] 2.10 (s, 3H, CH_3); 4.97 (t, 1H, C-3); 5.77 (d, 1H, C-2); 6.11 (d, 1H, NH); 6.57–7.81 (m, 14H, arom.H); $^3J_{23}$ = 10.0 Hz; $^3J_{3N}$ = 10.7 Hz
1c	1674	2155	3398	[a] 5.05 (t, 1H, C-3); 5.73 (d, 1H, C-2); 6.56–7.82 (m, 14H, arom.H); $^3J_{23}$ = 9.9 Hz; $^3J_{3N}$ = 10.1 Hz
1d	1674	2156	3406	[a] 5.01 (t, 1H, C-3); 5.74 (d, 1H, C-2); 6.55 (d, 1H, NH 6.68–7.81 (m, 14H, arom.H); $^3J_{23}$= 9.9 Hz; $^3J_{3N}$ = 10.3 Hz
1e	1674	2159	3392	[a] 2.08 (s, 3H, CH_3); 5.00 (t, 1H, C-3); 5.76 (d, 1H, C-2); 6.22 (d, 1H, NH); 6.56–7.81 (m, 14H, arom.H); $^3J_{45}$ = 11.2 H_z; $^3J_{45}$ = 12.0 Hz
1f	1675	2163	3381	[a] 5.10 (q, 1H, C-3); 5.41 (d, 1H, NH); 5.79 (d, 1H, C-2); 6.31–8.21 (m, 14H, arom.H); $^3J_{23}$= 9.8 Hz; $^3J_{3N}$ = 10.2 Hz
1g	1667 1677	2156	3317	[a] 5.27 (t, 1H, C-3); 6.18 (d, 1H, C-2); 6.58–7.60 (m, 14H, arom.H); 8.86 (d, 1H, NH); 12.81 (s, 1H, OH); $^3J_{23}$ = 9.5 Hz; $^3J_{3N}$ = 9.0 Hz
1h	1667 1677	2156	3316	
1i	1667 1677	2156	3315	[a] 2.14 (s, 3H, CH_3); 5.23 (t, 1H, C-3);); 6.14 (d, 1H, C-2); 6.57–8.03 (m, 13H, arom.H); 8.81(d, 1H, NH); 12.79 (s, 1H, OH); $^3J_{23}$ = 9.8 H_z; $^3J_{3N}$ = 9.0 Hz
1j	1667 1677	2156	3315	
1k	1668 1676	2158	3305	

	IR spectra (KBr) ($\tilde{\nu}$ in cm^{-1})			*^{1}H NMR data ([a] DMSO-d6 ; [b] $CDCl_3$) (δ in ppm)*
	$\nu_{C=O}$	ν_{SCN}	ν_{NH}	
3a	1642 1678	-	-	[b] 4.93 (d, 1 H, C-1); 6.69 (d, 1 H, C-2); 7.07–8.29 (m, 14H, arom.H); $^3J_{12}$ = 1.2 Hz
3b	1641 1678	-	-	[b] 2.32 (s, 3H, CH_3); 4.88 (d, 1H, C-1); 6.60 (d, 1H, C-2); 7.05–8.29 (m, 13H, arom.H); $^3J_{12}$ = 1.2 Hz
3c	1647 1682	-	-	[b] 2.32 (s, 3H, CH_3); 4.93 (d, 1H, C-1); 6.64 (d, 1H, C-2); 7.08–8.27 (m, 13H, arom.H); $^3J_{12}$ = 1.2 Hz
3d	1642 1678	-	-	[b] 1.20 (d, 6H, CH_3); 2.90 (m, 1H, CH); 4.87 (d, 1H, C-1); 6.62 (d, 1H, C-2); 7.05–8.28 (m, 13H, arom.H); $^3J_{12}$ = 1.2 Hz
3e	1644 1675	-	-	[b] 4.97 (d, 1H, C-1); 6.91 (d, 1H, C-5); 6.98–8.12 (m, 12H, arom.H); $^3J_{12}$ = 1.2 Hz

TABLE VII Analytical data of *trans* 5-aroyl-2-(aroylimino)-3,4-diarylthiazolidines **6**

6	R^1	R^2	R^3	R^4	*Yield (%)*	*Mp. (°C)*	*Empirical formula Molecular mass/ MS found*	*Analysis calculated/found (%)*			
								C	*H*	*N*	*S*
a	C_6H_5	C_6H_5	C_6H_5	4-CH_3-C_6H_4	58	185–187	$C_{30}H_{24}N_2O_2S$	75.60	5.08	5.88	6.73
							476.59/475	75.41	5.01	6.09	6.75
b	C_6H_5	C_6H_5	C_6H_5	4-NO_2-C_6H_4	53	191–193	$C_{29}H_{21}N_3O_4S$	68.62	4.17	8.28	6.32
							507.56/506	68.59	4.22	8.54	6.32
c	C_6H_5	C_6H_5	4-CH_3-C_6H_4	4-CH_3-C_6H_4	69	183–185	$C_{31}H_{28}N_2O_2S$	75.89	5.34	5.71	6.54
							490.62/489	75.79	5.23	5.88	6.53
d	C_6H_5	C_6H_5	4-CH_3-C_6H_4	4-NO_2-C_6H_4	61	189–190	$C_{30}H_{23}N_3O_4S$	69.08	4.44	8.06	6.15
							521.59/521	68.93	4.55	8.16	6.18
e	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-CH_3-C_6H_4	61	158–160	$C_{31}H_{28}N_2O_2S$	75.89	5.34	5.71	6.54
							490.62 /489	75.68	5.30	5.88	6.59
f	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-NO_2-C_6H_4	61	199–201	$C_{30}H_{23}N_3O_4S$	69.08	4.44	8.06	6.15
							521.59/520	69.01	4.47	8.26	6.18

TABLE VIII Analytical data of *trans* 5-aroyl-3,4-diaryl-2-(arylsulfenylimino)thiazolidines **7**

7	R^1	R^2	R^3	R^4	Yield (%)	Mp. (°C)	Empirical formula Molecular mass/ MS found	Analysis calculated/found (%)			
								C	H	N	S
a	C_6H_5	C_6H_5	C_6H_5	2-NO_2-C_6H_4	25	195–197	$C_{28}H_{21}N_3O_3S_2$	65.74	4.14	8.21	12.53
							511.61/511	65.77	4.32	8.47	12.54
b	C_6H_5	C_6H_5	4-CH_3-C_6H_4	2-NO_2-C_6H_4	26	194–196	$C_{29}H_{23}N_3O_3S_2$	66.27	4.41	7.99	12.20
							525.64/525	66.33	4.45	8.24	12.25
c	C_6H_5	C_6H_5	3-Cl-C_6H_4	2-NO_2-C_6H_4	13	89–93	$C_{28}H_{20}ClN_3O_3S_2$	61.59	3.69	7.70	11.74
							546.06/545	61.48	3.75	7.91	11.70
d	C_6H_5	C_6H_5	4-Cl-C_6H_4	C_6H_5	30	185–187	$C_{28}H_{21}ClN_2OS_2$	67.12	4.22	5.59	12.80
							501.06/500	67.05	4.28	5.85	12.63
e	C_6H_5	C_6H_5	4-Cl-C_6H_4	4-Cl-C_6H_4	46	172–174	$C_{28}H_{20}Cl_2N_2OS_2$	62.80	3.77	5.23	11.97
							535.50/534	62.61	3.78	5.42	11.89
f	C_6H_5	C_6H_5	4-Cl-C_6H_4	2-NO_2-C_6H_4	36	124–125	$C_{28}H_{20}ClN_3O_3S_2$	61.59	3.69	7.70	11.74
							546.06/545	61.46	3.91	7.66	11.69
g	C_6H_5	4-CH_3-C_6H_4	C_6H_5	2-NO_2-C_6H_4	49	172–174	$C_{29}H_{23}N_3O_3S_2$	66.27	4.41	7.99	12.20
							525.64/525	66.12	4.43	8.21	12.20
h	C_6H_5	4-Cl-C_6H_4	C_6H_5	2-NO_2-C_6H_4	45	178–179	$C_{28}H_{20}ClN_3O_3S_2$	61.59	3.69	7.70	11.74
							546.06/545	61.35	3.66	7.87	11.77

TABLE IX Analytical data of *trans* 5-aroyl-3,4-diaryl-2-(arylsulfonylimino)thiazolidines **8**

8	R^1	R^2	R^3	R^4	*Yield (%)*	*Mp. (°C)*	*Empirical formula Molecular mass/ MS found*	*Analysis calculated/found (%)*			
								C	*H*	*N*	*S*
a	C_6H_5	C_6H_5	C_6H_5	C_6H_5	54	170–171	$C_{28}H_{22}N_2O_3S_2$	67.45	4.45	5.62	12.86
							498.61/498	67.41	4.37	5.85	12.89
b	C_6H_5	C_6H_5	C_6H_5	4-CH_3-C_6H_4	70	190–191	$C_{29}H_{24}N_2O_3S_2$	67.95	4.72	5.46	12.51
							512.64/512	67.92	4.65	5.63	12.54
c	C_6H_5	C_6H_5	4-CH_3-C_6H_4	4-CH_3-C_6H_4	75	169–170	$C_{30}H_{26}N_2O_3S_2$	68.42	4.98	5.32	12.17
							526.67/526	68.36	4.85	5.52	12.23
d	C_6H_5	C_6H_5	4-CH_3-C_6H_4	4-NO_2-C_6H_4	15	208–210	$C_{29}H_{23}N_3O_5S_2$	62.46	4.16	7.53	11.50
							557.64/557	62.38	4.20	7.75	11.50
e	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-CH_3-C_6H_4	76	169–170	$C_{30}H_{26}N_2O_3S_2$	68.42	4.98	5.32	12.17
							526.67/526	68.42	4.92	5.49	12.19
f	C_6H_5	4-CH_3-C_6H_4	C_6H_5	4-$NO_2C_6H_4$	22	231–233	$C_{29}H_{23}N_3O_5S_2$	62.46	4.16	7.53	11.50
							557.64/557	62.54	4.14	7.71	11.48

TABLE X Spectroscopic data of the compounds **6**, **7** and **8**

	IR spectra (KBr) ($\tilde{\nu}$ *in* cm^{-1})			*^{1}H NMR data ([b] $CDCl_3$; [c] acetone-d_6) (δ in ppm)*	*^{13}C NMR data*
	$\nu_{C=O}$	$\nu_{s,SO2}$	$\nu_{s,NO2}$		
6a	1622 1678	-	-	[b] 2.34 (s, 3H, CH_3); 4.83 (d, 1H, C-4); 6.06 (d, 1H, C-5); 7.10–7.96 (m, 19H, arom.H); $^3J_{45}$ = 2.1 Hz	21.6(H_3); 53.2 (C-4); 66.1 (C-5); 126.7–142.7 (arom.C); 168.1 (C=N); 176.4 (C=O); 193.2 (C=O)
6b	1625 1678	-	1346	[c] 5.33 (d, 1H,C-4); 6.23 (d, 1H, C-5); 7.34–8.18 (m, 19H, arom.H); $^3J_{45}$ = 1.8 Hz	53.5 (C-4), 67.8 (C-5); 124.1–151.0 (arom.C); 170.6 (C=N); 174.5 (C=O); 194.4 (C=O)
6c	1629 1685	-	-	[c]2.32 (s, 3H, CH_3); 2.33 (s, 3H, CH_3); 5.21 (d, 1H, C-4); 6.15 (d, 1H, C-5); 7.14–8.11 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.1 (CH_3); 21.5 (CH_3); 53.5 (C-4); 67.3 (C-5); 127.5–143.4 (arom.C); 168.9 (C=N); 176.3 (C=O); 194.6(C=O)
6d	1628 1682	-	1347	[b] 2.37 (s, 3H, CH_3); 4.88 (d, 1H, C-4); 6.05 (d, 1H, C-5); 7.18–8.15 (m, 18H, arom.H); $^3J_{45}$ = 2.1 Hz	21.2 (CH_3) ; 52.9 (C-4); 66.7 (C-5); 123.1–150.0 (arom.C); 169.5 (C=N); 174.4 (C=O); 192.9 (C=O)
6e	1627 1679	-	-	[c]2.31 (s, 3H, CH_3); 2.32 (s, 3H, CH_3); 5.21 (d, 1H, C-4); 6.14 (d, 1H, C-5); 7.14–8.12 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.1 (CH_3); 21.5 (CH_3); 53.6 (C-4); 67.0 (C-5); 127.7–143.4 (arom.C); 168.9 (C=N); 176.2 (C=O); 194.6 (C=O)
6f	1629 1682	-	1343	[b] 2.32 (s, 3H, CH_3); 4.90 (d, 1H, C-4); 6.05 (d, 1H, C-5); 7.15–8.14 (m, 18H, arom.H); $^3J_{45}$ = 2.1 Hz	21.1 (CH_3); 52.9 (C-4), 66.4 (C-5); 123.1–149.8 (arom.C); 169.5 (C=N); 174.2 (C=O); 192.9 (C=O)
7a	1693	-	1334	[b] 4.91 (d, 1H, C-4); 6.05 (d, 1H, C-5); 7.13–8.25 (m, 19H, arom.H); $^3J_{45}$ = 2.75 Hz	52.7 (C-4); 68.3 (C-5); 124.0–143.0 (arom.C); 162.1 (C=N); 192.5 (C=O)
7b	1683	-	1328	[b] 2.31 (s, 3H, CH_3); 4.88 (d, 1H, C-4); 6.00 (d, 1H, C-5); 7.13–8.26 (m, 18H, arom.H); $^3J_{45}$ = 2.75 Hz	21.0 (CH_3); 52.6 (C-4); 68.5 (C-5); 124.0–143.3 (arom.C); 163.0 (C=N); 192.6 (C=O)
7c	1674	-	1335	[b] 4.90 (d, 1H, C-4); 6.04 (d, 1H, C-5); 7.14–8.28 (m, 18H, arom.H); $^3J_{45}$ = 2.75 Hz	52.8 (C-4); 67.7 (C-5); 123.2–142.4 (arom.C); 160.1 (C=N); 192.3 (C=O)
7d	1677	-	-	[b] 4.85 (d, 1H, C-4); 5.99 (d, 1H, C-5); 7.11–7.89 (m, 19H, arom.H); $^3J_{45}$ = 2.75 Hz	52.7 (C-4); 68.4 (C-5); 124.6–139.1 (arom.C); 161.6 (C=N); 192.5 (C=O)

	IR spectra (KBr) ($\tilde{\nu}$ in cm^{-1})			*^1H NMR data ([b] $CDCl_3$; [c] acetone-d_6) (δ in ppm)*	*^{13}C NMR data*
	$\nu_{C=O}$	$\nu_{s,SO2}$	$\nu_{s,NO2}$		
7e	1677	-	-	[b] 4.85 (d, 1H, C-4); 5.99 (d, 1H, C-5); 7.11–7.89 (m, 18H, arom.H); $^3J_{45}$ = 2.75 Hz	52.7 (C-4); 68.4 (C-5); 124.6–139.1 (arom.C); 161.6 (C=N); 192.5 (C=O)
7f	1686	-	1335	[b] 4.90 (d, 1H, C-4); 5.99 (d, 1H, C-5); 7.15–8.32 (m, 18H, arom.H); $^3J_{45}$ = 2.75 Hz	52.7 (C-4); 68.1 (C-5); 124.2–142.6 (arom.C); 161.5 (C=N); 192.4 (C=O)
7g	1683	-	1331	[b] 2.36 (s, 3H, CH_3); 4.89 (d, 1H,C-4); 6.03 (d, 1H, C-5); 7.15–8.34 (m, 18H, arom.H); $^3J_{45}$ = 2.74 Hz	21.1 (CH_3) 52.8 (C-4); 68.2 (C-5); 124.0–143.1 (arom.C); 162.3 (C=N); 192.6 (C=O)
7h	1682	-	1328	[b] 4.87 (d, 1H, C-4); 6.03 (d, 1H, C-5); 7.14–8.25 (m, 18H, arom.H); $^3J_{45}$ = 3.05 Hz	52.6 (C-4); 67.6 (C-5); 124.1–142.8 (arom.C); 161.5 (C=N); 192.2 (C=O)
8a	1683	1151	-	[c] 5.37 (d, 1H, C-4); 6.07 (d, 1H, C-5); 7.32–8.06 (m, 20H, arom.H); $^3J_{45}$ = 1.8 Hz	53.2 (C-4); 68.9 (C-5); 127.1 –145.4 (arom.C); 166.8 (C=N); 193.9 (C=O)
8b	1688	1153	-	[c] 2.37 (s, 3H, CH_3); 5.36 (d, 1H, C-4); 6.08 (d, 1H, C-5); 7.20–8.08 (m, 19H, arom.H); $^3J_{45}$ = 1.8 Hz	21.4 (CH_3); 53.1 (C-4); 68.8 (C-5); 127.1–143.5 (arom.C); 166.5 (C=N); 193.8 (C=O)
8c	1687	1146	-	[c] 2.26 (s, 3H, CH_3); 2.37 (s, 3H, CH_3); 5.34(d, d, 1 H, C-4); 6.04 (d, 1 H, C-5); 7.11–8.06 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.0 (CH_3) ; 21.4 (CH_3); 53.1 (C-4); 68.9 (C-5); 127.2–143.5 (arom.C); 166.5 (C=N); 193.9 (C=O)
8d	1688	1153	1345	[c] 2.28 (CH_3); 5.41 (d, 1 H, C-4); 6.08 (d, 1 H, C-5); 7.16–8.27 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.0 (CH_3); 53.3 (C-4); 69.4 (C-5); 124.8–148.8 (arom.C); 167.8 (C=N); 193.7 (C=O)
8e	1685	1148	-	[c] 2.31 (s, 3H, CH_3); 2.36 (s, 3H, CH_3); 5.32 (d, 1 H, C-4); 6.02 (d, 1 H, C-5); 7.19–8.06 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.1 (CH_3); 21.4 (CH_3); 53.2 (C-4); 68.7 (C-5); 127.2–143.5 (arom.C); 166.5 (C=N); 193.9 (C=O)
8f	1688	1153	1346	[c] 2.32 (s, 3H, CH_3); 5.41 (d, 1H, C-4); 6.07 (d, 1H, C-5); 7.21–8.29 (m, 18H, arom.H); $^3J_{45}$ = 1.8 Hz	21.1 (CH_3); 53.4 (C-4); 69.2 (C-5); 124.8–148.0 (arom.C); 167.6 (C=N); 193.7 (C=O)

EXPERIMENTAL

Melting points were determined with a Boetius micro heating stage (Carl Zeiss Jena) without correction. Elementary analyses were performed by a CHNS-932 LECO analyser. IR spectra were recorded on a 205FT-IR spectrophotometer. Mass spectra were taken on an AMD 402–3 spectrometer (Intectra GmbH) and ^{1}H NMR and ^{13}C NMR spectra with an AC 250 spectrometer (Bruker) using TMS as internal reference. The X-ray diffraction data were collected with a Siemens P4 four-circle diffractometer with Mo-K_{α}-radiation ($\lambda = 0.71073$ Å) and a graphite monochromator in routine ω-scan. The observation criterion was in all cases $I \geqq 2\sigma(I)$.

threo 1,3-Diaryl-3-arylamino-2-thiocyanatopropanones 1

α-Thiocyanatoacetophenone (50 mmol) is dissolved in methanol (100 mL). Equimolar amounts of aromatic aldehyde and amine are added. Than the mixture is stirred at room temperature until the product is precipitated. The reaction is completed by standing for further 8 to 12 h. The crude product is filtered off, washed with ethanol and recrystallized from acetone (Table IV).

trans 5-Aroyl-3, 4-diarylthiazolidine-2-iminium chlorides 2

Dry hydrogen chloride is bubbled through a suspension of the corresponding 1,3-diaryl-3-arylamino-2-thiocyanatopropanone **1a-1f** (10 mmol) in dry chloroform (50 mL) for 15 to 30 min. The precipitated salt **2** is filtered off, washed with dry diethyl ether and used in the next reactions without purification.

trans 2-Aroyl-1-aryl-1, 2-dihydro-thiazolo[3, 2-a]quinazoline-5-ones 3

Dry hydrogen chloride is bubbled through a suspension of the corresponding β-amino α-thiocyanato ketone **1g-1k** (5 mmol) in anhydrous chloroform (25 mL) for 30 min at room temperature. Than the reaction solution is heated under reflux for 1 h. The crystalline product is filtered off and resuspended in water (100 mL). The reaction mixture is neutralized with potassium hydrogen carbonate, stirred for 1 h at 50 °C and allowed to

stand at room temperature for 8 to 12 h. The crude product is filtered off, washed with water and recrystallized from ethanol/acetone mixtures (Table V).

trans 5-Aroyl-2-(aroylimino)-3, 4-diarylthiazolidines 6

Triethylamine (5 mmol) and the corresponding benzoyl chloride (2.5 mmol) are added to a suspension of thiazolidine-2-iminium chloride **2** (2.5 mmol) in dry acetone (50 mL). The reaction mixture is heated under reflux for 3 h and than poured into water (200 mL). The precipitate is filtered off, washed with water and recrystallized from ethanol/acetone (Table VII).

trans 5-Aroyl-3, 4-diaryl-2-(arylsulfenylimino)thiazolidines 7

The corresponding thiazolidine-2-iminium chloride **2** (2.5 mmol) is suspended in dry chloroform (25 mL) and anhydrous triethylamine (5 mmol) is added. Than a solution of the respective arenesulfenyl chloride in dry chloroform (25 mL) is added dropwise at room temperature. After addition, the mixture is stirred for 10 to 15 h. The solution is washed with water, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The residue is purified by recrystallization from ethanol/acetone (Table VIII).

trans 5-Aroyl-3, 4-diaryl-2-(arylsulfonylimino)thiazolidines 8

The respective thiazolidine-2-iminium chloride **2** (2.5 mmol) is suspended in dry acetone (50 mL). Triethylamine (5 mmol) and than the arenesulfonyl chloride (2.5 mmol) are added. The mixture is refluxed for 3 h and than poured into water (200 mL). The crude prduct is filtered off, washed with water and recrystallized from ethanol/acetone (Table IX).

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