SYNTHESIS OF SOME NEW 8-QUINOLINYLOXY-5-SULFONAMIDE DERIVATIVES

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5-Sulfonyl-8-quinolinol[1] was used for the synthesis of various derivatives. This attempt was directed by knowledge that 8-quinolinol was utilized in the synthesis of biologically active heterocycles as bactericides, fungicides and bioregulators[2 – 4].

The biological and pesticidal activity of 1,3,4-oxadiazoles[5 – 7], as well as the pharmacological interest of the quinoline moiety, are well known, too.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H NMR spectra were measured on EM-360 90 MHz spectrometer using TMS as an internal standard. IR spectra were recorded in KBr on a Pye–Unicam SP 200-G spectrometer. Elemental analyses were determined on a Perkin–Elmer 240 C microanalyzer.

5,8-Disubstituted Quinolines *I*; General Procedure

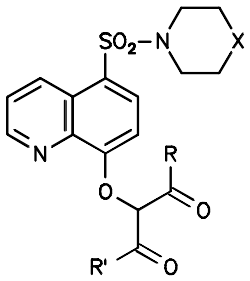
Equimolar quantities of 2-chloro malonic acid derivative (0.01 mol) was added to an alcoholic sodium salt of 5-piperidino(morpholino)sulfonyl-8-quinolinol and the reaction mixture was heated under reflux for 5 h. The precipitated product was filtered off, washed with water and recrystallized from ethanol.

5,8-Disubstituted Quinolines *II – IV*; General Procedure

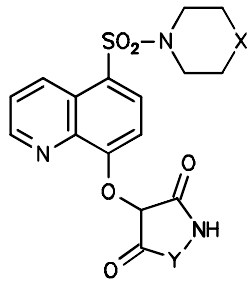
A mixture of *I* (0.001 mol) and hydrazine hydrate (0.001 mol) or phenylhydrazine (0.001 mol) in an alcoholic sodium ethoxide solution (0.04 g of sodium in 10 ml ethanol) was refluxed on a water bath for 8 h. The reaction mixture was filtered off, the filtrate was cooled and neutralized with acetic acid. The product was crystallized from ethanol.

5,8-Disubstituted Quinolines *V – VII*; General Procedure

A mixture of *I* (0.001 mol), hydroxylamine hydrochloride (0.0025 mol) and pyridine (10 ml) was refluxed for 5 h. The reaction mixture was cooled, neutralized with hydrochloric acid and product recrystallized from methanol.



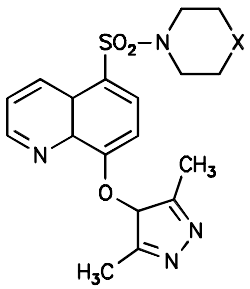
I



II

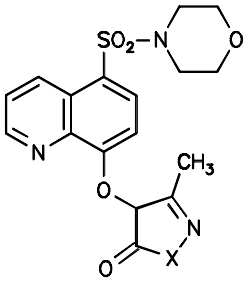
I	X	R	R'
a	CH_2	OC_2H_5	OC_2H_5
b	CH_2	CH_3	CH_3
c	O	OC_2H_5	OC_2H_5
d	O	CH_3	CH_3
e	O	CH_3	OC_2H_5

II	X	Y
a	CH_2	NH
b	CH_2	$N-C_6H_5$
c	O	NH
d	O	$N-C_6H_5$
Va	CH_2	O
Vb	O	O

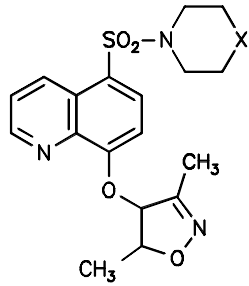


IIIa, X = CH_2

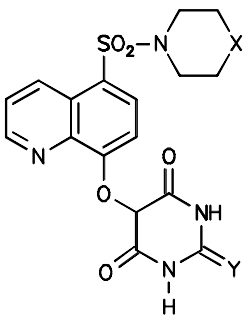
IIIb, X = O



IVa X = NH
IVb X = N–C_6H_5
VI X = O

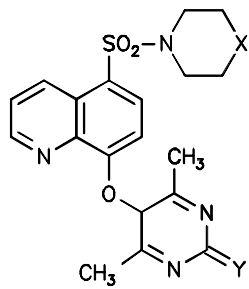


VIIa X = CH_2
VIIb X = O



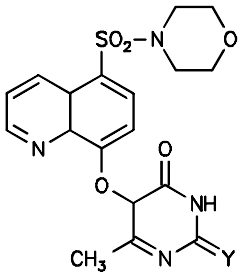
VIII

VIII	X	Y
a	CH_2	O
b	O	O
c	CH_2	S
d	O	S

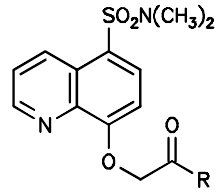


IX

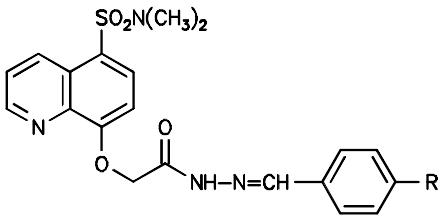
IX	X	Y
a	CH_2	O
b	O	O
c	CH_2	S
d	O	S



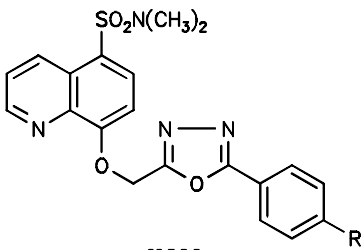
Xa Y = O
Xb Y = S



XIa R = OC_2H_5
XIb R = $NH-NH_2$

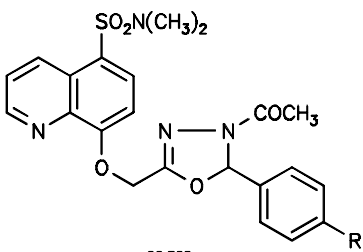


XII

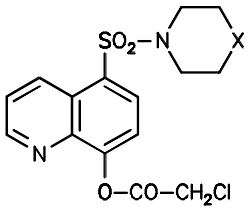


XIII

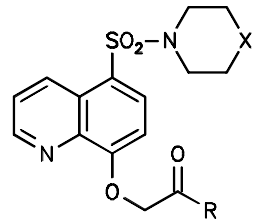
XII, XIII, XIV	R
a	H
b	***p***-CH_3
c	***p***-OCH_3
d	***p***-NO_2
e	***p***-OH
f	***o***-OH



XIV

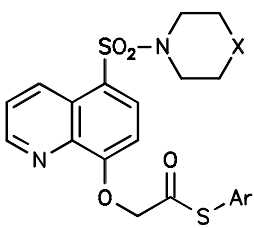


XVIa, X = CH_2
XVIb, X = O

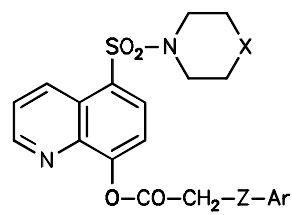


XVII

XVII	X	R
a	CH_2	OH
b	O	OH
c	CH_2	Cl
d	O	Cl



XVIII

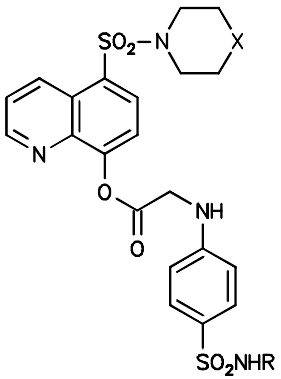


XIX, *XX*

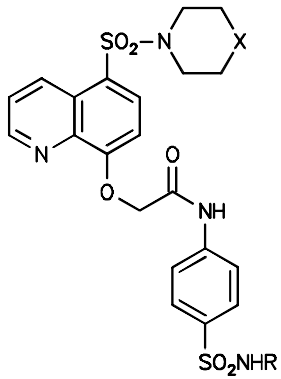
XIX Z = S
XX Z = SO_2

In formulae *XVIII–XX*:

	X	Ar
a	CH_2	*p*-$CH_3C_6H_4$
b	O	*p*-$CH_3C_6H_4$
c	CH_2	$-CH_2C_6H_5$
d	O	$-CH_2C_6H_5$
e	CH_2	*p*-ClC_6H_4
f	O	*p*-ClC_6H_4
g	CH_2	benzimidazolyl
h	O	benzimidazolyl
i	CH_2	2-benzo
j	O	2-benzo

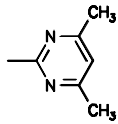


XXI



XXII

In formulae *XXI*, *XXII*:

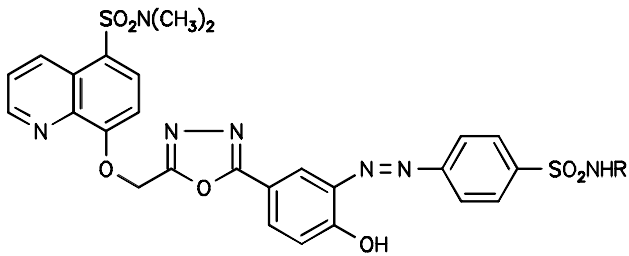
	X	R
a	CH_2	H
b	O	
c	CH_2	$COCH_3$
d	O	
e	CH_2	$C(NH_2)=NH$
f	O	
g	CH_2	
h	O	
i	CH_2	
j	O	
k	CH_2	
l	O	

5,8-Disubstituted Quinolines *VIII* – *X*; General Procedure

A mixture of *I* (0.001 mol), urea or thiourea (0.001 mol) in an alcoholic sodium ethoxide (0.02 g Na in 10 ml of ethanol) was heated under reflux on a water bath for 7 h. The reaction mixture was cooled, neutralized with hydrochloric acid and the precipitate was filtered off, washed with water, collected and recrystallized from ethanol.

Ethyl (5-Dimethylaminosulfonyl-8-quinolinyloxy)acetate (*XIa*)

A mixture of 5-dimethylaminosulfonyl-8-hydroxyquinoline (0.01 mol), ethyl chloroacetate (0.01 mol) and fused sodium acetate (3 g) in ethanol (100 ml) was refluxed for 6 h. On cooling, the crystalline solid thus formed was collected and recrystallized from ethanol.



XV

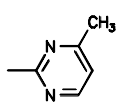
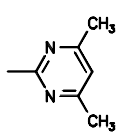
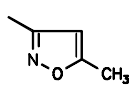
XV	R
a	–H
b	–$COCH_3$
c	–$C(=NH)NH_2$
d	
e	
f	
g	
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TABLE I
Physical and analytical data of the synthesized compounds

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
Ia[b]	283 – 285 75	$C_{21}H_{26}N_2O_7S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 720 (CO)	4.2 m, 4 H (2 CH_2); 1.6 t, 6 H 92 CH_3); 2.6 – 3.6 m, 10 H (pip); 7.5 – 7.7 m, (arom CH)
Ib[b]	>340 66	$C_{19}H_{22}N_2O_5S$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 720 (CO)	1.9 s, 6 H (2 CH_3); 7.6 – 7.8 m, 6 H (arom + CH); 2.7 – 3.8 m, 10 H (pip)
Ic	311 – 313 80	$C_{20}H_{24}N_2O_8S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 710 (CO)	
Id[b]	315 – 317 71	$C_{18}H_{20}N_2O_6S$	1 360 (SO_2 asym), 1 150 (SO2 sym), 1 730 (CO)	1.92 s, 6 H (2 CH_3); 7.4 – 7.7 m, 6 H (arom + CH); 2.6 – 3.7 m, 8 H (morph)
Ie[b]	306 – 308 63	$C_{19}H_{22}N_2O_7S$	1 350 (SO_2 asym), 1 160 (SO_2 sym), 1 725 (CO)	4.3 m, 2 H (CH_2); 1.6 t, 3 H (CH_3); 2.1 s, 3 H (CH_3CO); 7.6 – 7.9 m, 6 H (arom + CH); 2.5 – 3.6 m, 8 H (morph)
IIa	206 – 208 74	$C_{17}H_{18}N_4O_5S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 710 (CO), 3 150 (NH)	
IIb[c]	310 – 312 78	$C_{23}H_{22}N_4O_5S$	1 360 (SO_2 asym), 1 150 SO_2 sym), 1 720 (CO), 3 190 (NH)	9.75 s, 1 H (NHCO); 7.3 s, 1 H (CH pyrazol); 7.7 m, 10 H (arom); 2.6 – 3.5 m, 10 H (pip)
IIc	>340 75	$C_{16}H_{16}N_4O_6S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 700 (CO), 3 200 (NH)	
IId[c]	302 – 304 79	$C_{22}H_{20}N_4O_6S$	1 365 (SO_2 asym), 1 160 (SO_2 sym), 1 710 (CO), 3 170 (NH)	8.8 s, 1 H (NHCO); 7.4 s, 1 H (CH pyrazol); 3.0 – 3.5 m, 8 H (morph); 7.6 – 7.8 m, 10 H (arom)
Va[c]	303 – 305 66	$C_{17}H_{17}N_3O_6S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 700 (CO), 3 150 (NH)	9.0 s, 1 H (NH); 7.5 s, 1 H (COCHCO); 2.6 – 3.7 m, 10 H (pip); 7.4 – 7.7 m, 5 H (arom)
Vb	>340 68	$C_{16}H_{15}N_3O_7S$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 700 (CO), 3 170 (NH)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^{1}H NMR δ, ppm
IIIa[b]	>340 72	$C_{19}H_{22}N_4O_3S$	1 360 (SO_2 asym), 1 165 (SO_2 sym), 1 600 (NC)	1.8 s, 6 H (2 CH_3); 7.5 s, 1 H (CH pyrazol); 7.8 m, 5 H (arom); 2.7 – 3.6 m, 10 H (pip)
IIIb[b]	246 – 248 75	$C_{18}H_{20}N_4O_4S$	1 365 (SO_2 asym), 1 160 (SO_2 sym), 1 580 (NC)	1.6 s, 6 H (2 CH_3); 7.6 s, 1 H (CH pyrazol); 7.6 m, 5 H (arom); 3.6 m, 8 H (morph)
IVa	223 – 225 70	$C_{17}H_{18}N_4O_5S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 3 150 (NH), 1 600 (NC)	
IVb	>340 72	$C_{23}H_{22}N_4O_5S$	1 365 (SO_2 asym), 1 165 (SO_2 sym), 1 700 (CO), 1 600 (NC)	
VI[c]	>340 66	$C_{17}H_{17}N_3O_6S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 720 (CO), 1 600 (NC)	1.9 s, 3 H (CH_3 isoxazol); 7.8 s, 1 H (CH isoxazol); 7.6 m, 5 H (arom); 3.1 – 3.6 m, 8 H (morph)
VIIa[b]	298 – 300 71	$C_{19}H_{21}N_3O_4S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 600 (NC)	1.9 s, 6 H (2 CH_3 isoxazol); 2.8 – 3.9 m, 10 H (pip); 7.3 – 7.5 m, 5 H (arom)
VIIb[b]	308 – 310 74	$C_{18}H_{19}N_3O_5S$	1 355 (SO_2 asym); 1.150 (SO_2 sym), 1 600 (NC)	1.94 s, 6 H (2 CH_3 isoxazol); 7.6 m, 5 H (arom); 3.0 – 3.5 m, 8 H (morph)
Xa	>340 64	$C_{18}H_{18}N_4O_6S$	1 365 (SO_2 asym), 1 160 (SO_2 sym), 1 715 (CO), 3 130 (NH)	
Xb[b]	>340 61	$C_{18}H_{18}N_4O_5S_2$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 730 (CO), 3 100 (NH)	1.8 s, 3 H (CH_3); 9.6 s, 1 H (NH); 7.5 – 7.8 m, 6 H (arom); 3.1 – 3.6 m, 8 H (morph)
VIIIa[b]	296 – 298 66	$C_{18}H_{18}N_4O_6S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 700 (CO), 3 120 (NH)	8.1 s, 2 H (2 NH); 7.5 – 7.7 m, 6 H (arom); 2.7 – 3.4 m, 10 H (pip)
VIIIb	328 – 330 63	$C_{17}H_{16}N_4O_7S$	1 360 (SO_2 asym), 1 165 (SO_2 sym), 1 720 (CO), 3 150 (NH)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
VIIIc[b]	316 – 318 61	$C_{18}H_{18}N_4O_5S_2$	1 360 (SO_2 asym), 1 150 (SO_2 sym), 1 730 (CO), 3 130 (NH)	8.4 s, 2 H (2 NH); 7.3 – 7.65 m, 6 H (arom); 2.6 – 3.6 m, 10 H (pip)
VIIId	>340 64	$C_{17}H_{16}N_4O_6S_2$	1 365 (SO_2 asym), 1 150 (SO_2 sym), 1 710 (CO), 3 150 (NH)	
IXa[b]	323 – 325 68	$C_{20}H_{22}N_4O_4S$	1 360 (SO_2 asym), 1 165 (SO_2 sym)	1.95 s, 6 H (2 CH_3); 7.4 – 7.8 m, 6 H (arom); 2.5 – 3.4 m 10 H (pip)
IXb	>340 62	$C_{19}H_{20}N_4O_5S$	1 365 (SO_2 asym), 1 155 (SO_2 sym)	
IXc[b]	>340 65	$C_{19}H_{20}N_4O_4S_2$	1 365 (SO_2 asym), 1 165 (SO_2 sym)	1.92 s, 6 H (2 CH_3), 7.5 – 7.8 m, 6 H (arom); 2.7 – 3.4 m, 10 H (pip)
IXd[b]	>340 50	$C_{19}H_{20}N_4O_4S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym)	1.94 s, 6 H (2 CH_3); 7.5 – 7.7 m, 6 H (arom); 3.1 – 3.7 m, 8 H (morph)
XIa[b]	>340 88	$C_{15}H_{18}N_2O_5S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 730 (C=O)	7.0 – 7.6 m, 5 H (arom); 4.6 s, 2 H (CH_2); 4.17 q, 2 H (CH_2 ester); 1.6 t, 3 H (CH_3 ester); 3.1 s, 6 H (2 CH_3)
XIb	238 – 240 85	$C_{13}H_{16}N_4O_4S$	3 260, 3 100 ($NHNH_2$), 1 690 (C=O), 1 355 (SO_2 asym), 1 160 (SO_2 sym)	
XIIa[b]	318 – 320 78	$C_{20}H_{20}N_4O_4S$	3 140 (NH), 1 680 (C=O), 1 600 (C=N), 1 360 (SO_2 asym), 1 155 (SO_2 sym)	7.2 – 7.8 m, 10 H (arom); 9.0 s, 1 H (ArCH=N–); 4.5 s, 2 H (CH_2); 3.2 s, 6 H (2 CH_3)
XIIb	196 – 198 81	$C_{21}H_{22}N_4O_4S$	3 150 (NH), 1 690 (C=O), 1 600 (C=N), 1 350 (SO_2 asym), 1 160 (SO_2 sym)	
XIIc[b]	300 – 302 76	$C_{21}H_{22}N_4O_5S$	3 150 (NH), 1 680 (C=O), 1 600 (C=N), 1 360 (SO_2 asym), 1 160 (SO_2 sym)	7.2 – 7.6 m, 9 H (arom); 9.1 s, 1 H (ArCH=N–); 4.3 s, 2 H (CH_2); 3.1 s, 6 H (CH_3); 3.7 s, 3 H (OCH_3)

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^{1}H NMR δ, ppm
XIId[b]	310 – 312 78	$C_{20}H_{19}N_5O_6S$	3 140 (NH), 1 690 (C=O), 1 600 (C=N), 1 360 (SO_2 asym), 1 160 (SO_2 sym)	7.1 – 7.5 m, 9 H (arom); 9.0 s, 1 H (ArCH=N–); 4.6 s, 2 H (CH_2); 3.3 s, 6 H (2 CH_3)
XIIe	304 – 306 74	$C_{20}H_{20}N_4O_5S$	3 360 (OH), 3 150 (NH), 1 680 (C=O), 1 600 (C=N), 1 355 (SO_2 asym), 1 160 (SO_2 sym)	
XIIf	294 – 296 71	$C_{20}H_{20}N_4O_5S$	3 350 (OH), 3 130 (NH), 1 690 (C=O), 1 600 (C=N), 1 360 (SO_2 asym), 1 160 (SO_2 sym)	
XIIIa[b]	309 – 311 64	$C_{20}H_{18}N_4O_4S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N)	4.5 s, 2 H (CH_2); 3.2 s, 6 H (2 CH_3), 7.2 – 7.8 m, 10 H (arom)
XIIIb	320 – 322 67	$C_{21}H_{20}N_4O_4S$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=-N)	
XIIIc[b]	315 – 317 65	$C_{21}H_{20}N_4O_5S$	1 355 (SO_2 asym), 1 150 (SO_2 sym), 1 590 (C=N)	4.3 s, 2 H (CH_2); 3.1 s, 6 H (2 CH_3); 3.8 s, 3 H (OCH_3); 7.7 – 7.8 m, 9 H (arom)
XIIId[b]	326 – 328 70	$C_{20}H_{17}N_5O_6S$	1 360 (SO_2 asym); 1 160 (SO_2 sym); 1 600 (C=N)	5.1 s, 2 H (CH_2); 3.3 s, 6 H (2 CH_3); 7.4 – 8.1 m, 9 H (arom)
XIIIe	312 – 314 68	$C_{20}H_{18}N_4O_5S$	3 450 (OH), 1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N)	
XIIIf	305 –307 66	$C_{20}H_{18}N_4O_5S$	3 400 (OH), 1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 540 (C=N)	
XIVa[b]	278 – 280 60	$C_{22}H_{22}N_4O_5S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 590 (C=N), 1 700 (C=O)	5.2 s, 2 H (CH_2); 3.1 s, 6 H (2 CH_3); 4.0 s, 3 H ($COCH_3$); 7.1 – 8.0 m, 11 H (arom)

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^{1}H NMR δ, ppm
XIVb	178 – 180 62	$C_{23}H_{24}N_4O_5S$	1 360 (SO_2 asym), 1 155 (SO_2 sym), 1 595 (N=C), 1 710 (C=O)	
XIVc[b]	136 – 138 80	$C_{23}H_{24}N_4O_6S$	1 360 (SO_2 asym), 1 150 (SO_2 sym), 1 600 (C=N), 1 700 (C=O)	5.4 s, 2 H (CH_2); 3.2 s, 6 H (2 CH_3); 3.8 s, 3 H (OCH_3); 7.2 – 8.1 m, 10 H (arom), 4.1 s, 3 H ($COCH_3$)
XIVd[b]	296 – 298 63	$C_{22}H_{21}N_5O_7S$	1 350 (SO_2 asym), 1 150 (SO_2 sym), 1 600 (C=N), 1 720 (C=O)	5.6 s, 2 H (CH_2); 3.4 s, 6 H (2 CH_3); 3.9 s, 3 H (CH_3) 7.3 – 8.3 m, 10 H (arom)
XIVe	290 – 292 61	$C_{22}H_{22}N_4O_6S$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 585 (C=N), 1 710 (CO), 3 400 (OH)	
XVa	143 – 145 dec. 67	$C_{26}H_{23}N_7O_7S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N), 1 580 (N=N), 3 100 (NH), 3 450 (OH)	
XVb[c]	268 – 270 dec. 70	$C_{28}H_{25}N_7O_8S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N), 1 580 (N=N), 3 100 (NH), 1 720 (C=O), 3 400 (OH)	5.4 s, 2 H (CH_2); 3.1 s, 6 H (2 CH_3); 4.3 s, 3 H ($COCH_3$); 11.4 s, 1 H (OH); 9.5 s, 1 H (NH); 6.8 – 8.1 m, 12 H (arom)
XVc	243 – 245 dec. 80	$C_{27}H_{25}N_9O_7S_2$	1 355 (SO_2 asym), 1 160)SO_2 sym), 1 600 (C=N), 1 585 (N=N), 3 200, 3 340 (NH_2), 3 450 (OH)	
XVd[c]	258 – 260 dec. 68	$C_{30}H_{25}N_9O_7S_2$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N), 1 580 (N=N), 3 100 (NH), 3 400 (OH)	5.2 s, 2 H (CH_2); 3.0 s, 6 H (2 CH_3); 11.2 s, 1 H (OH); 9.5 s, 1 H (NH); 6.9 – 8.0 m, 15 H (arom
XVe[c]	292 – 294 dec 74	$C_{31}H_{27}N_9O_7S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N), 1 585 (N=N), 3 100 (NH), 3 430 (OH)	5.5 s, 2 H (CH_2); 3.2 s, 6 H (2 CH_3); 2.9 s, 3 H (CH_3); 11.2 s, 1 H (OH); 9.5 s, 1 H (NH); 7.1 – 8.2 m, 14 H arom)

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^{1}H NMR δ, ppm
XVf	340 70	$C_{32}H_{29}N_9O_7S_2$	1 300 (SO_2 asym), 1 150 (SO_2 sym), 1 600 (C=N), 1 580 (N=N), 3 150 (NH), 3 450 (OH)	
XVg	125 – 127 65	$C_{12}H_{26}N_2O_7S$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 600 (C=N), 1 580 (N=N), 3 100 (NH), 3 400 (OH)	
XVh[c]	145 – 147 85	$C_{29}H_{24}N_8O_7S_3$	1 360 (SO_2 asym), 1 150 (SO_2 sym), 1 600 (C=N), 1 585 (N=N), 3 150 (NH), 3 430 (OH)	5.4 s, 2 H (CH_2); 3.3 s, 6 H (2 CH_3); 9.4 s, 1 H (OH); 7.0 – 8.1 m, 14 H (arom)
XVIa	260 85	$C_{16}H_{17}ClN_2O_4S$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 1 710 (CO)	
XVIb	315 87	$C_{15}H_{15}ClN_2O_5S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 695 (CO)	
XVIIa	312 84	$C_{16}H_{18}N_2O_5S$	1 365 (SO_2 asym), 1 170 (SO_2 sym), 3 045 (CH arom), 2 950 (CH aliph)	
XVIIb	305 82	$C_{15}H_{16}N_2O_6S$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 3 040 (CH arom), 2 930 (CH aliph)	
XVIIc	310 85	$C_{16}H_{17}ClN_2O_4S$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 3 050 (CH arom), 2 940 (CH aliph)	
XVIId	320 83	$C_{15}H_{15}ClN_2O_5S$	1 360 (SO_2 asym), 1 170 (SO_2 sym), 3 040 (CH arom), 2 930 (CH aliph)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XVIIIa[c]	265 74	$C_{23}H_{24}N_2O_4S_2$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 3 040 (CH arom), 2 920 (CH aliph), 1 690 (CO), 700 (CS)	2.5 s, 3 H (CH_3); 2.6 – 3.6 m, 10 H (pip), 7.1 – 8.5 m, 9 H (arom); 4 00 s, 2 H (CH_2)
XVIIIb[c]	298 71	$C_{22}H_{22}N_2O_5S_2$	1 360 (SO_2 asym), 1 170 (SO_2 sym), 3 050 (CH arom), 2 940 (CH aliph), 1 700 (CO), 710 (CS)	2.4 s, 3 H (CH_3); 3.1 – 3.6 m, 8 H (morph); 7.3 – 8.2 m, 9 H (arom); 3.8 s, 2 H (CH_2)
XVIIIc	237 73	$C_{23}H_{24}N_2O_4S_2$	1 370 (SO_2 asym), 1 165 (SO_2 sym), 3 040 (CH arom), 2 950 (CH aliph), 1 690 (CO), 700 (CS)	
XVIIId	225 70	$C_{22}H_{22}N_2O_5S_2$	1 360 (SO_2 asym), 1 170 (SO_2 sym), 3 050 (CH arom), 2 930 (CH aliph), 1 710 (CO)	
XVIIIe[b]	215 72	$C_{22}H_{21}ClN_2O_4S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 700 (CO)	4.0 s, 2 H (CH_2); 2.6 – 3.5 m, 10 (pip); 7.1 – 8.6 m, 9 H (arom)
XVIIIf[b]	190 75	$C_{21}H_{19}ClN_2O_5S_2$	1 355 (SO_2 asym), 1 150 (SO_2 sym), , 1 690 (CO)	3.0 – 3.5 m, 8 H (morph); 4.0 s, 2 H (CH_2); 6.8 – 8.4 m 9 H (arom)
XVIIIg	198 78	$C_{23}H_{22}N_4O_4S_2$	3 445 (NH), 3 050 (CH arom), 3 000 (CH aliph), 1 710 (CO), 1 600 (C=N), 700 (CS)	
XVIIIh	270 73	$C_{22}H_{20}N_4O_5S_2$	3 430 (NH), 3 040 (CH arom), 2 950 (CH aliph), 1 700 (CO), 1 600 (C=N), 700 (CS)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XVIIIi	275 76	$C_{23}H_{21}N_3O_4S_3$	3 015 (CH arom), 2 980 (CH aliph), 1 700 (CO), 1 630 (C=N), 700 (CS)	
XVIIIj	280 70	$C_{22}H_{19}N_3O_5S_3$	3 030 (CH arom), 2 960 (CH aliph), 1 700 (CO), 1 610 (C=N), 720 (CS)	
XIXa[c]	165 75	$C_{23}H_{24}N_2O_4S_2$		2.6 s, 3 H (CH_3); 2.7 – 3.6 m, 10 H (pip); 7.2 – 8.4 m, 9 H (arom); 3.9 s, 2 H (CH_2)
XIXb	145 78	$C_{22}H_{22}N_2O_5S_2$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 1 680 (CO), 710 (CS)	
XIXc	292 70	$C_{23}H_{24}N_2O_4S_2$	1 365 (SO_2 asym), 1 165 (SO_2 sym), 1 690 (CO), 700 (CS)	
XIXd	220 72	$C_{22}H_{22}N_2O_5S_2$	1 360 (SO_2 asym), 1 170 (SO_2 sym), 1 680 (CO), 710 (CS)	
XIXe[c]	260 68	$C_{22}H_{21}ClN_2O_4S_2$		2.6 – 3.6 m, 10 H (pip); 4.00 s, 2 H (CH_2); 7.2 – 8.4 m, 9 H (arom)
XIXf	190 76	$C_{21}H_{19}ClN_2O_5S_2$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 690 (CO), 700 (CS)	
XIXg	265 80	$C_{23}H_{22}N_4O_4S_2$	3 450 (NH), 3 050 (CH arom), 3 000 (CH aliph), 1 710 (CO), 1 600 (C=N) 700 (CS)	
XIXh	295 72	$C_{22}H_{20}N_4O_5S_2$	3 440 (NH), 3 030 (CH arom), 2 980 (CH aliph), 1 700 (CO), 1 600 (C=N) 700 (CS)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XIXi[b]	178 74	$C_{23}H_{21}N_3O_4S_3$	1 365 (SO_2 asym), 1 165 (CH aliph), 1 720 (CO)	2.6 – 3.6 m, 10 H (pip); 3.9 s, 2 H (CH_2); 6.8 – 8.3 m, 9 H (arom); 9.5 s, 1 H (NH)
XIXj[b]	162 70	$C_{22}H_{19}N_3O_5S_3$	1 355 (SO_2 asym), 1 160 (SO_2 sym), 1 710 (CO)	3.0 – 3.6 m, 8 H (morph); 3.9 s, 2 H (CH_2); 7.0 – 8.5 m, 9 H (arom)
XXa	227 72	$C_{23}H_{24}N_2O_6S_2$	3 040 (CH arom), 2 960 (CH aliph), 1 700 (CO)	
XXb	192 73	$C_{22}H_{22}N_2O_7S_2$	3 030 (CH arom), 3 000 (CH aliph), 1 700 (CO)	
XXc	275 76	$C_{23}H_{24}N_2O_6S_2$	3 040 (CH arom), 2 930 (CH aliph), 1 700 (CO), 1 170, 1 370, 1 400 (SO_2)	
XXd	225 74	$C_{22}H_{22}N_2O_7S_2$	3 050 (CH arom), 2 950 (CH aliph), 1 700 (CO), 710 (CS), 1 170, 1 360, 1 420 (SO_2)	
XXe	205 70	$C_{22}H_{21}ClN_2O_6S_2$	3 020 (CH arom), 2 930 (CH aliph), 1 695 (CO)	
XXf	128 77	$C_{21}H_{19}ClN_2O_7S_2$	3 040 (CH arom), 2 950 (CH aliph), 1 700 (CO)	
XXg	198 82	$C_{23}H_{22}N_4O_6S_2$	3 050 (CH arom), 2 960 (CH aliph), 1 710 (CO), 3 400 (NH), 1 600 (C=N)	
XXh	115 75	$C_{22}H_{20}N_4O_7S_2$	3 030 (CH arom), 2 950 (CH aliph), 1 700 (CO), 3 430 (NH), 1 600 (C=N)	

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XXi	189 78	$C_{23}H_{21}N_3O_6S_3$	3 040 (CH arom), 2 980 (CH aliph), 1 690 (CO), 1 600(C=N)	
XXj	178 72	$C_{22}H_{19}N_3O_7S_3$	3 050 (CH arom), 2 960 (CH aliph), 1 700 (CO), 1 600 (C=N)	
XXIa	268 73	$C_{22}H_{24}N_4O_6S_2$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 1 690 (CO), 3 350, 3250 (NH_2)	
XXIb	228 65	$C_{21}H_{22}N_4O_7S_2$	1 360 (SO_2 asym), 1 165 (SO_2 sym), 1 700 (CO), 3 400 (NH)	
XXIc[b]	252 72	$C_{24}H_{26}N_4O_7S_2$	1 365 (SO_2 asym), 1 170 (SO_2 sym), 1 680, 1 700 (CO), 3 330 (NH)	4.0 s, 2 H (CH_2), 3.4 s, 3 H (CH_3), 2.5 – 3.6 m, 10 H (pip); 9.3 s, 1 H (NH); 7.3 – 8.2 m, 9 H (arom)
XXId[b]	263 63	$C_{23}H_{24}N_4O_8S_2$	1 355 (SO_2 asym), 1 170 (SO_2 sym), 1 690, 1 710 (CO), 3 350 (NH)	
XXIe	160 72	$C_{23}H_{26}N_6O_6S_2$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 450, 3 240 (NH_2)	
XXIf	245 70	$C_{22}H_{24}N_6O_7S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 680 (CO), 3 430, 3 220 (NH_2)	
XXIg[c]	258 73	$C_{26}H_{26}N_6O_6S_2$	1 370 (SO_2 asym), 1 170 (SO_2 sym), 1 695 (CO), 3 220 (NH)	3.8 s, 2 H (CH_2); 2.6 – 3.5 m, 10 H (pip); 9.6 s, 1 H (NH); 7.1 – 8.1 m, 12 H (arom)

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XXIh	235 75	$C_{25}H_{24}N_6O_7S_2$	1 360 (SO_2 asym), 1 170 (SO_2 sym), 1 690 (CO), 3 250 (NH)	
XXIi	305 65	$C_{28}H_{30}N_6O_6S_2$	1 360 (SO_2 asym), 1 160 (SO_2 sym), 1 700 (CO), 3 180 (NH)	
XXIj	187 73	$C_{27}H_{28}N_6O_7S_2$	1 365 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 210 (NH)	
XXIk[c]	180 68	$C_{25}H_{25}N_5O_6S_3$	1 380 (SO_2 asym), 1 160 (SO_2 sym), 1 690 (CO), 3 190 (NH)	3.9 s, 2 H (CH_2), 2.6 – 3.6 m, 10 H (pip); 9.8 s, 1 H (NH); 7.3 – 8.2 m, 11 H (arom)
XXIl	285 71	$C_{24}H_{23}N_5O_7S_3$	1 390 (SO_2 asym), 1 175 (SO_2 sym), 1 700 (CO), 3 210 (NH)	
XIIa	210 76	$C_{22}H_{24}N_4O_6S_2$	1 375 (SO_2 asym), 1 165 (SO_2 sym), 1 685 (CO), 3 450, 3 250 (NH_2)	
XXIIb	167 68	$C_{21}H_{22}N_4O_7S_2$	1 380 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 420, 3 220 (NH_2)	
XXIIc	212 74	$C_{24}H_{26}N_4O_7S_2$	1 390 (SO_2 asym), 1 165 (SO_2 sym), 1 695, 1 710 (CO), 3 420 (NH)	
XXIId[c]	175 65	$C_{23}H_{24}N_4O_8S_2$	1 375 (SO_2 asym), 1 180 (SO_2 sym), 1 680, 1 700 (CO), 3 430 (NH)	4.0 s, 2 H (CH_2); 3.0 s, 3 H (CH_3); 3.2 – 3.6 m, 8 H (morph), 7.1 – 8.2 m, 9 H (arom)

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula[a] M.w.	IR ν, cm^{-1}	^1H NMR δ, ppm
XXIIe	254 75	$C_{23}H_{26}N_6O_6S_2$	1 380 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 460, 3 250 (NH_2)	
XXIIf	178 72	$C_{22}H_{24}N_6O_7S_2$	1 365 (SO_2 asym), 1 180 (SO_2 sym), 1 680 (CO), 3 440, 3 230 (NH_2)	
XXIIg[c]	276 76	$C_{26}H_{26}N_6O_6S_2$	1 375 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 460, 3 250 (NH)	4.0 s, 2 H (CH_2); 9.8 s, 1 H (NH); 2.6 – 3.5 m, 10 H (pip); 7.2 – 8.3 m, 12 H (arom)
XXIIh	285 78	$C_{25}H_{24}N_6O_7S_2$	1 370 (SO_2 asym), 1 165 (SO_2 sym), 1 710 (CO), 3 240 (NH)	
XXIIi	292 70	$C_{28}H_{30}N_6O_6S_2$	1 380 (SO_2 asym), 1 170 (SO_2 sym), 1 695 (CO), 3 190 (NH)	
XXIIj	192 76	$C_{27}H_{28}N_6O_7S_2$	1 365 (SO_2 asym), 1 170 (SO_2 sym), 1 700 (CO), 3 220 (NH)	
XXIIk[c]	209 72	$C_{25}H_{25}N_5O_6S_3$	1 375 (SO_2 asym), 1 160 (SO_2 sym), 1 695 (CO), 3 190 (NH)	4.0 s, 2 H (CH_2); 2.6 – 3.5 m, 10 H (pip); 9.7 s, 1 H (NH); 7.2 – 8.1 m, 11 H (arom)
XXIIl	200 74	$C_{24}H_{23}N_5O_7S_3$	1 385 (SO_2 asym), 1 175 (SO_2 sym), 1 700 (CO), 3 220 (NH)	

[a] Elemental analysis of CHNS gave results equal to those calculated within experimental error. NMR measured in [b] $(CD_3)_3SO$; [c] $CDCl_3$.

5-Dimethylaminosulfonyl-8-quinolinyloxyacethydrazide (*XIb*)

A mixture of *XIa* (0.01 mol) and hydrazine hydrate (0.01 mol) in absolute ethanol (50 ml) was refluxed for 4 h. The reaction mixture was cooled in an ice bath and diluted with water (50 ml). The precipitate was filtered off and recrystallized from benzene.

N^1-Benzylidene-(5-dimethylaminosulfonyl-8-quinolinyloxymethyl) Carbohydrazides *XII*

A mixture of *XIb* (0.01 mol) and respective aromatic aldehyde (0.01 mol) in ethanol (50 ml) was refluxed for 2 h. The precipitate formed on cooling was collected and recrystallized from ethanol.

2-Aryl-5-(5-dimethylaminosulfonyl-8-quinolinoxymethyl)-1,3,4-oxadiazoles *XIII*

A mixture of *XII* (0.01 mol), anhydrous sodium acetate (0.01 mol) and glacial acetic acid (20 ml) was heated under reflux for 3 h. The reaction mixture was concentrated and cooled. The precipitated product was filtered off, dried and crystallized from ethanol.

4-Acetyl-5-aryl-2-(5-dimethylaminosulfonyl-8-quinolinyloxymethyl)-1,3,4-oxadiazolines *XIV*

A mixture of *XIII* (0.01 mol) and acetic anhydride (5 ml) was heated under reflux for 1 h. Excess of acetic anhydride and acetic acid was distilled off under reduced pressure and the residue was recrystallized from ethanol.

General Method for the Synthesis of Azo Compounds *XV*

4-Substituted benzenesulfamoyldiazonium chlorides were prepared by diazotization of 0.05 mol of 4-aminobenzenesulfonyl derivatives, dissolved in a mixture of water (20 ml) and HCl (3 ml) with sodium nitrite at 5 °C. The diazonium chlorides were used immediately, without separation, for the synthesis of the corresponding azo compounds.

To a solution of *XIIIe* (0.01 mol) in sodium hydroxide solution (40 ml, 20%), the appropriate diazonium salt was added portionwise with stirring. The temperature was maintained at 5 °C, and stirring was continued for 1 h. The reaction mixture was kept at ambient temperature for a further 1 h, during which time the product precipitated. This was filtered, washed with water, dried and recrystallized from benzene.

Preparation of Chloroacetates *XVI*

A solution of 5-piperidino(morpholino)sulfonyl-8-quinolinol[1] (0.01 mol) was dissolved in dry pyridine (100 ml) and chloroacetyl chloride (0.01 mol) was added dropwise. The reaction mixture was stirred for 4 h at room temperature. The precipitate was filtered off and recrystallized from petroleum ether.

Preparation of Compounds *XVII*

A solution of 5-piperidino(morpholino)-8-quinolinol (0.01 mol) was dissolved in alcoholic potassium hydroxide (0.56 g KOH in 30 ml absolute ethanol), then chloroacetic acid (0.01 mole was added portionwise. The solution was heated under reflux for 10 h, then cooled and acidified with dilute hydrochloric acid (5 ml concentrated HCl in 20 ml H_2O). The precipitate was filtered off and recrystallized from ethanol to yield *XVIIa* or *XVIIb*, respectively.

A mixture of the acid *XVIIa* or *XVIIb*, respectively (0.01 mol) was dissolved in dry benzene (50 ml) and thionyl chloride (3 ml) was added. The reaction mixture was heated under reflux for 5 h.

The excess of solvent and thionyl chloride was removed under reduced pressure and the precipitate was recrystallized from petroleum ether to give *XVIIc* or *XVIId*, respectively.

Preparation of Compounds *XVIII – XX*

5-Sulfonamido-8-chloroacetoxyquinoline and/or 5-sulfonamido-8-quinolinoxyacetyl chloride was dissolved in 30 ml of dry benzene. To the solution of *XVIa* or *XVIb*, respectively the arylmercaptan (0.01 mol) was added portionwise and the mixture was heated under reflux for 10 h. The solvent was removed under reduced pressure and the products *XVIII* were recrystallized from ethanol.

Similarly compounds *XIX* were prepared from *XVIIc* or *XVIId*, respectively.

α-Mercaptoacetates *XIX* (0.01 mol) were dissolved in glacial acetic acid (25 ml) and the calculated volume of hydrogen peroxide was added dropwise. The reaction mixture was left 72 h at room temperature, then poured into ice cold water and the products *XX* were recrystallized from dioxane.

Preparation of Sulfonamides *XXI* and *XXII*

Compounds *XVIa*, *XVIb*, *XVIIc* or *XVIId* (0.01 mol) and 4-amino-4′-substituted benzene sulfonamides (0.01 mol) in dry benzene (20 ml) were heated under reflux for 8 h. The solvent was removed under reduced pressure and the products were recrystallized from ethanol.

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