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Vicarious Nucleophilic Substitution of Hydrogen, Bisannulation and Competitive Reactions of α-Haloalkyl Carbanions with Bicyclic Azaaromatic Compounds

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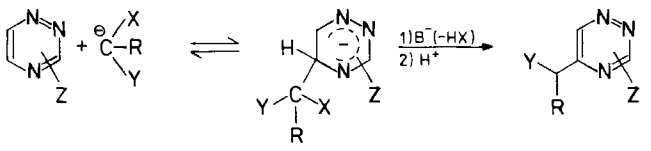
Carbanions of α-haloalkyl aryl sulfones, sulfonates, and sulfonamides react with bicyclic heteroaromatic compounds (quinoxalines, naphthyridines, and 5-azaquinoxalines) according to two general pathways: vicarious nucleophilic substitution of hydrogen and/or bisannulation. In some cases other competitive reactions such as S_NAr are observed. Factors governing the direction of these reactions are discussed in terms of the charge distribution in the anionic σ adducts and the reaction conditions.

Carbanions with a leaving group X at the carbanionic center can replace hydrogen in electrophilic aromatic and heteroaromatic compounds, particularly in nitroarenes. This reaction, named "Vicarious Nucleophilic Substitution of Hydrogen" (VNS), proceeds by addition of the carbanion to nitroarenes in the *ortho*- or *para*-positions bearing hydrogen, followed by base-induced β-elimination of HX[2-4]. This process is of general character with respect to nitroarenes and carbanions. Many electrophilic heterocycles without a nitro group such as 1,2,4-triazine[5,6], benzothiazole[5a,6], pteridine[6b,7] etc. also undergo this reaction as exemplified by the reaction of a 1,2,4-triazine derivative in Scheme 1.

Scheme 1



X: leaving group, Y: carbanion stabilizing group

However, some bicyclic heterocycles such as quinoxalines and naphthyridines react with α-halo carbanions in a different way to afford bisannulated products[8]. The dramatic difference in the course of the reaction of 1,2,4-triazines, pteridines, etc. on the one hand and quinoxalines on the other hand may be rationalized by taking into account the degree of the negative charge delocalization in the intermediate σ adducts. In these adducts of the carbanions with quinoxaline the charge is mainly located on the vicinal nitrogen atom, which therefore acquires highly nucleophilic properties. Since in this situation the base-induced β-elimination is hindered, an intramolecular S_N2-type reaction leading to mono- and subsequently to bisannulation occurs. Modification of the substrate structure by the introduction of such substituents into the quinoxaline ring, which promote more efficient charge delocalization favours the VNS[9], or even provides possibilities to control the reaction course[10].

In this paper we give a comprehensive account of our studies on the reactions of some bicyclic heterocycles such as quinoxalines, 1,*x*-naphthyridines (*x* = 5, 6, 7, 8), and 5-azaquinoxalines (pyrido[2,3-*b*]pyrazines) with α-halo sulfones, α-haloalkanesulfonamides, and α-haloalkanesulfonic acid esters of general structure $XCHR^1SO_2Y$ **1**–**8** (Table 1), which, for stability reasons[11], have been used as carbanion precursors.

Table 1. Carbanion precursors

	$XCHR^1SO_2Y$		
1	$ClCH_2SO_2Ph$	**5**	$ClCH_2SO_2$Morpholino
2	$ClCH_2SO_2NMe_2$	**6**	$ClCH_2SO_2Tol$
3	$ClCH_2SO_3CH_2tBu$	**7**	$ClCH(Me)SO_2Ph$
4	$ClCH_2SO_2tBu$	**8**	$BrCH_2SO_2Tol$

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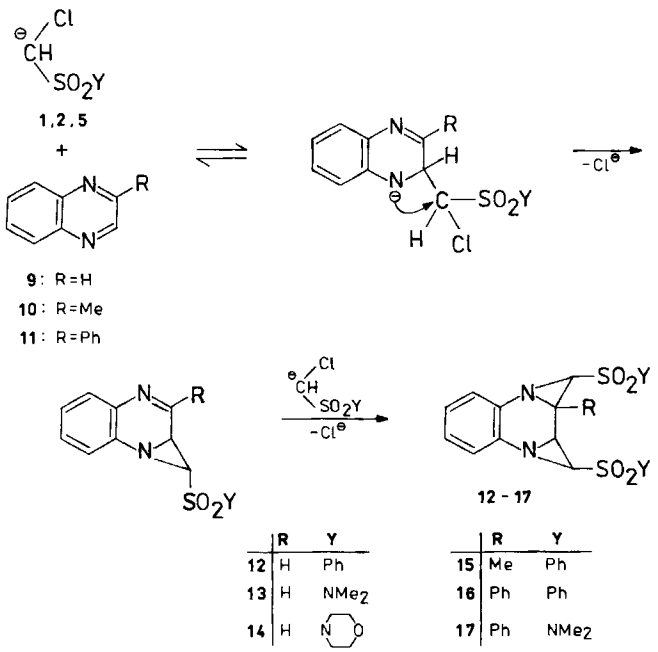
Quinoxalines and Quinoxalinones

In our preliminary communication we have reported that carbanions of chloromethyl phenyl sulfone (**1**) and chloromethanesulfonamides (**2, 5**) react with quinoxaline (**9**) and 2-phenylquinoxaline (**11**) to give exclusively bisannulated derivatives[8]. Other quinoxaline derivatives as for example 2-methylquinoxaline (**10**) react in the same way (Table 2). In all cases no traces of the monoannulated intermediate products can be detected, even when equimolar amounts of the carbanion precursor and quinoxaline are used or the reaction is stopped at low conversion. This indicates, that the second step, the addition of the carbanion to the aliphatic imine bond, is faster than the first one, in which the aromaticity of the quinoxaline is destroyed. The formation of **12**–**17** is analogous to the aza-Darzens condensation of α-halo carbanions with imines, which till now has only been known in the aliphatic series[12].

Scheme 2



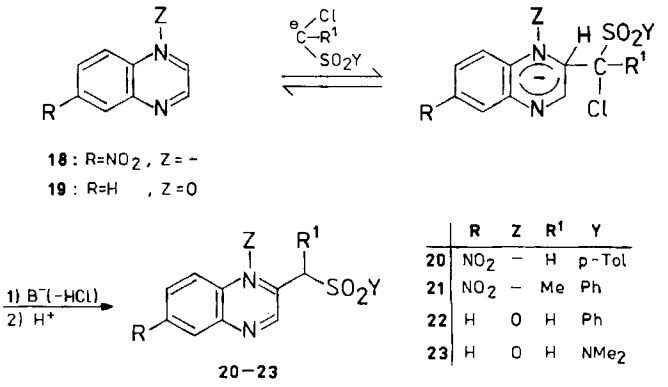
In all these cases even no traces of the VNS products in the reaction mixtures have been detected either. Independently, we have made many attempts to promote β-elimination in the anionic σ adducts, which are necessary intermediates for both reactions, by changing the reaction conditions (e.g. low temperature, less ionizing solvents, less efficient leaving group, counterions forming more covalent bonds, high concentration of strong bases)[10], but without success.

On the other hand, an introduction of a nitro group into position 6 of the carbocyclic ring of quinoxaline (**18**) or oxidation to the mono *N*-oxide (**19**) assures efficient delocalization of the negative charge in the corresponding σ adducts. Thus, the elimination leading to the VNS products **20**–**23** becomes the only process (Scheme 3). Since formation of the quinoxaline *N*-oxide and reduction of the *N*-oxide function are facile processes, this reaction sequence offers the possibility of introducing functionalized substituents into the quinoxaline ring by the VNS reaction.

Table 2. Reactions of quinoxaline derivatives with $XCHR^1SO_2Y$ (Schemes 2–4)

Starting materials		Procedure	Product	Yield (%)
9	**1**	A	**12**	66
9	**2**	A	**13**	62
9	**5**	A	**14**	75
10	**1**	A	**15**	87
11	**1**	A	**16**	65
11	**2**	A	**17**	87
18	**6**	A	**20**	73
18	7	A	**21**	58
19	**1**	A	**22**	62
19	**2**	A	**23**	53
24	**1**	A	**25a**	36
24	**2**	A	**25b**	30
24	**5**	A	**25c**	32
26	**1**	A	**28a**	10
			29a	49
			25a	15
26	**1**	C	**28a**	55
			25a	7
26	**8**	C	**29d**	55
27	**1**	A	**28a** + **25a**	30
			29a	62
27	**1**	C	**28a**	55
			29a + **25a**	7

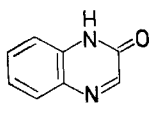
Scheme 3



Surprisingly, 2(1*H*)-quinoxalinone (**24**), which under strongly basic conditions exists in form of the corresponding anion, is able to react with the carbanions of chloromethyl phenyl sulfone (**1**) and the chloromethanesulfonamides **2**, **5** according to the annulation pathway to give the corresponding tricyclic derivatives **25a**–**c**, but with only moderate yields (30–36%).

We have already reported on some examples of the reactions of carbanions with negatively charged molecules[13]; for obvious reasons some difficulties are encountered in such processes.

Of particular interest are the reactions of the α-halo carbanions with 2-chloro- and 2-methoxyquinoxaline (**26**, **27**;



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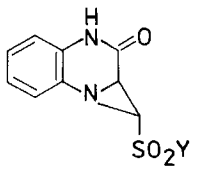


25a-c

Table 2, Scheme 4). In this case three major processes can be anticipated. Addition to C-2 producing σ^{Cl} or σ^{OMe} adducts is assumed to give S_NAr substitution products, whereas σ^H adducts, generated as a result of the addition to C-3, can react further according to two pathways – β-elimination of HX leading to the substitution of hydrogen or intramolecular substitution of groups X yielding annulated products. In fact, however, an elimination has again not been observed, and the three types of the products **25**, **28**, and **29** formed in these processes result from S_NAr substitution and a combination of annulation and S_NAr. The results are illustrated in Scheme 4 and compiled in Table 2.

Intramolecular nucleophilic substitution in the initial adduct **A** gives a monoaziridine, which rapidly reacts with another carbanion molecule to afford finally **29** or hydrolyzes to **25**. Higher temperature and/or a better leaving group X (Br instead of Cl) favor this pathway. The intramolecular substitution is decelerated at lower temperature and when X = Cl; thus, due to the reversibility of the formation of the σ^H adduct **A** the S_NAr process occurring via the σ^L adduct dominates.

This indicates that addition of the carbanion to C-3 bearing the hydrogen atom is faster than to the halogen-substituted C-2. This result once again confirms the general rule concerning the relative rates of the nucleophilic addition to electrophilic aromatic rings[14].

Naphthyridines

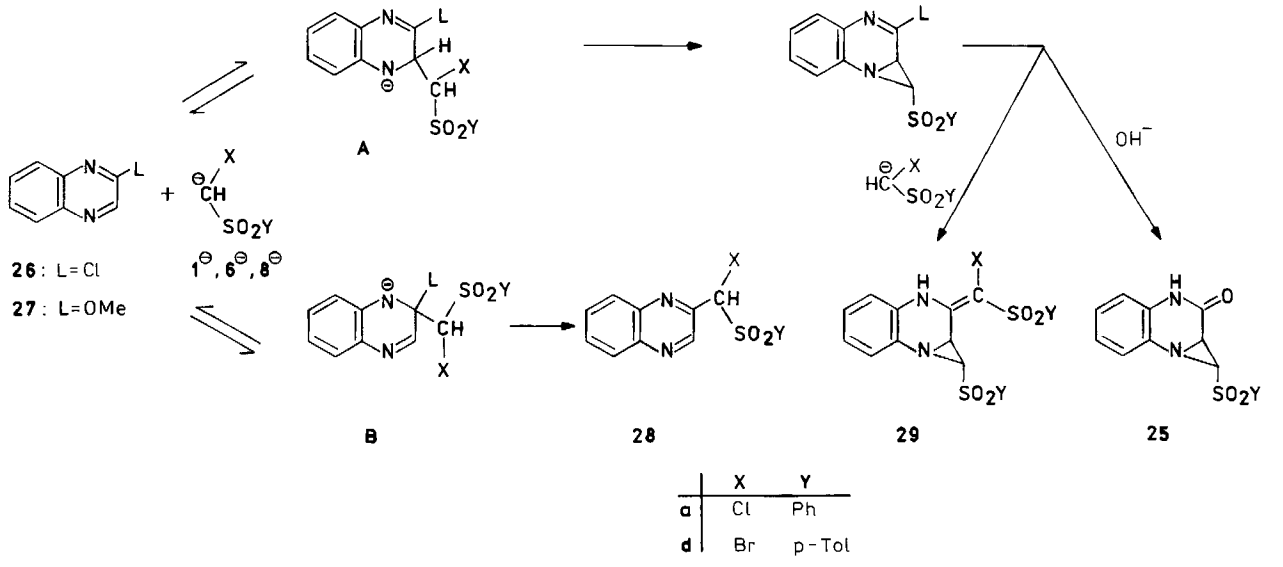
Similarly to quinoxalines, naphthyridines react with **1** according to the bisannulation scheme[8]. With other α-halo carbanions (2^-, 3^-) 1,5-, 1,6-, 1,7-, and 1,8-naphthyridines (**30**–**33**), as well 2- and 4-methyl-1,8-naphthyridines (**34**, **35**), also react according to the bisannulation pathway with formation of products with cyclopropane and aziridine rings annulated to the naphthyridine skeleton (Scheme 5, Table 3).

Table 3. Reactions of naphthyridine derivatives with the carbanions of $ClCH_2SO_2Y$ (Scheme 5, Procedure A)

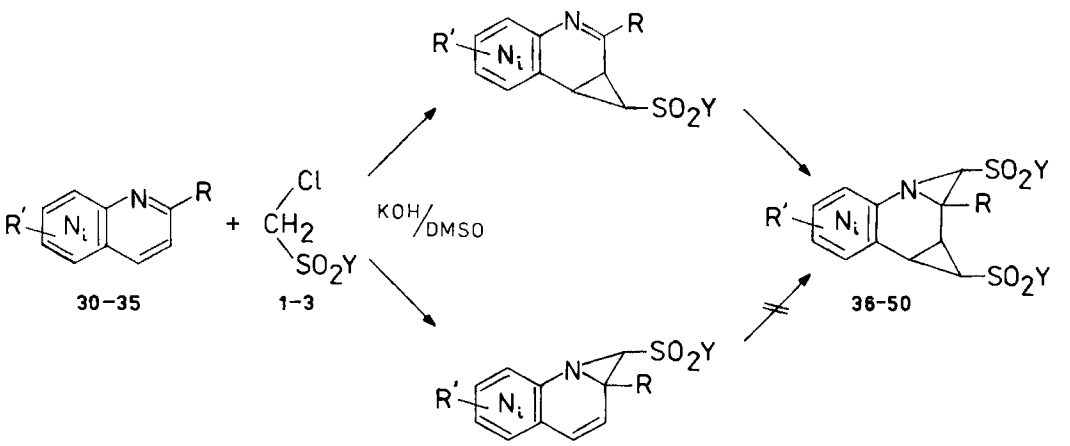
Starting materials		Position of N_i	Products R	R′	Y	No	Yield (%)
30	**1**	7-	H	H	Ph	**36**	40
30	**2**	7-	H	H	NMe_2	**37**	35
30	**3**	7-	H	H	OCH_2tBu	**38**	25
31	**1**	6-	H	H	Ph	**39**	59
31	**2**	6-	H	H	NMe_2	**40**	48
31	**3**	6-	H	H	OCH_2tBu	**41**	23
32	**1**	5-	H	H	Ph	**42**	77
32	**2**	5-	H	H	NMe_2	**43**	48
32	**3**	5-	H	H	OCH_2tBu	**44**	42
33	**1**	4-	H	H	Ph	**45**	66
33	**2**	4-	H	H	NMe_2	**46**	32
33	**3**	4-	H	H	OCH_2tBu	**47**	40
34	**1**	4-	H	5-Me	Ph	**48**	23
		4-	1b-Me	H	Ph	**49**	51
35	**1**	4-	H	7-Me	Ph	**50**	41

It can be supposed that the overall process of bisannulation of 1,*x*-naphthyridines involves initial addition of the carbanion at C-4 with formation of a cyclopropane ring followed by fast formation of the aziridine ring. Scheme 5 also shows that the alternative pathway – initial formation of the aziridine ring – would produce a monoannulated intermediate, which is unable to react with the carbanion. This reasoning is supported by selective annulation of these naphthyridine rings, in which addition in the γ-position with

Scheme 4



Scheme 5



	N_i	R	R′
30	5-	H	H
31	6-	H	H
32	7-	H	H

	N_i	R	R′
33	8-	H	H
34	8-	Me	H
35	1-	H	4-Me

respect to nitrogen is possible, and by the inertness of 2,6-naphthyridine where such possibility does not exist. The latter has been completely recovered after treating with the carbanion of **1**.

The selective reaction of **1** with 4-methyl-1,8-naphthyridine (**35**) in the nonsubstituted ring yielding **50** is in good agreement with the above discussion, as well as the nonselective reaction of **1** with 2-methyl-1,8-naphthyridine (**34**) giving products **48** and **49**. In the latter case the reaction proceeds with participation of each of the rings.

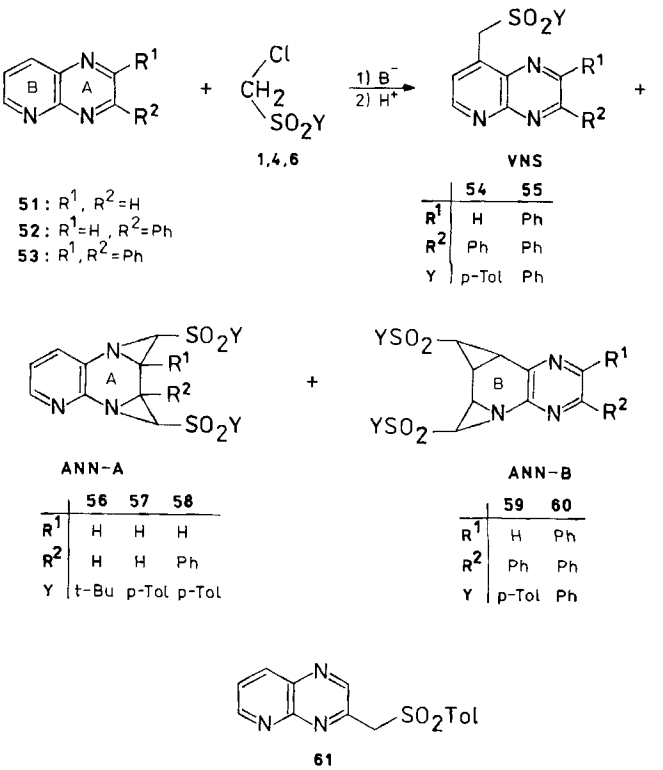
5-Azaquinoxalines

We have proved that effective charge delocalization in the intermediate anionic σ adducts is the main prerequisite for the VNS reaction course. Such long-lived adducts susceptible of β-elimination give VNS products exclusively, as demonstrated for 6-nitroquinoxaline (**18**) and quinoxaline *N*-oxide (**19**).

Earlier, using 6-azaquinoxaline as a model compound, we have also demonstrated, that the introduction of a third nitrogen atom into the bicyclic aromatic system also favors β-elimination leading to the VNS[10], due to the better charge distribution in the σ adduct. Now, for the same purpose, some 5-azaquinoxaline (pyrido[2,3-*b*]pyrazine) derivatives **51**–**53** have been studied.

However, in the heterogeneous KOH/DMSO system compound **51** reacts with **4** and **6** only according to the bisannulation pathway, giving products in which the three-membered rings are fused to the pyrazine fragment. In the σ adducts of the carbanions to 3-phenyl and 2,3-diphenyl-5-azaquinoxaline derivatives **52** and **53** the negative charge is more efficiently delocalized so that under analogous conditions the annulation is accompanied by the formation of small quantities of the VNS products **54** and **55**. In the case of **52** and **53** use of strong and well-soluble bases such as *t*BuOK causes the reaction to be entirely shifted toward the elimination leading to VNS products, whereas in the case of **51** in order to obtain the VNS product we had to work at low temperature, using a large excess of *t*BuOK, as described earlier[10].

Scheme 6



51: R^1, R^2 = H
52: R^1 = H, R^2 = Ph
53: R^1, R^2 = Ph

	54	**55**
R^1	H	Ph
R^2	Ph	Ph
Y	p-Tol	Ph

	56	**57**	**58**
R^1	H	H	H
R^2	H	H	Ph
Y	t-Bu	p-Tol	p-Tol

	59	**60**
R^1	H	Ph
R^2	Ph	Ph
Y	p-Tol	Ph

61

Some Aspects of the NMR Spectra of the Bisannulated Products

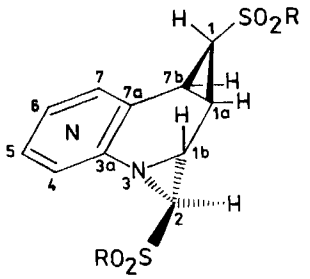
Since in the formation of the bisannulated products at least four new asymmetric centers are created quite a few stereoisomers could be expected to be produced. Nevertheless, we have observed the formation of one diastereoisomer only, in which interactions between substituents are minimized. At the beginning of our research work we have pro-

Table 4. Reactions of 5-azaquinoxaline derivatives with chloromethyl sulfones (Scheme 6)

Quinoxaline	Conditions	Products (and ratio, %) VNS	ANN-A	ANN-B	Total yield (%)
51	KOH/DMSO	–	**56** (100)	–	67
51	KOH/DMSO	–	**57** (100)	–	32
51	*t*BuOK/NH_3 −65°C	**61**[a] (90)	**57** (10)	–	41
52	KOH/DMSO	**54** (14)	**58** (37)	**59** (49)	57
52	*t*BuOK/DMF −20°C	**54** (100)	–	–	41
52	*t*BuOK/DMSO 20°C	**54** (100)	–	–	50
53	KOH/DMSO	**55** (24)	–	**60** (76)	62

[a] VNS in the pyrazine ring.

posed such a structure **C** on the basis of the ^{1}H-NMR data, which in several cases has later been confirmed by X-ray investigations[15–17].



C

For all compounds examined, coupling between 1a-H and 1b-H protons has not been observed[18]. According to the Karplus and Conroy equation[19] such coupling only occurs when the dihedral angle between C–H bonds is close to 90°. Hence, the three-membered rings must assume opposite directions with respect to the six-membered tetrahydrogenated ring. Coupling constants for cyclopropane or aziridine rings also confirm such geometry of the molecule. For example, for the cyclopropane ring of **37** we have observed a large (J = 9.2 Hz; *cis*) and two moderate ($J \approx 4.5$ Hz, *trans*) coupling constants. This has allowed us to assign the chemical shift to the 1-H proton and also to establish the configuration at the C-1 carbon. In this way it is impossible to assign the chemical shifts of the two remaining hydrogens (1a-H, 7b-H), of the cyclopropane ring.

Observed values of J for all cyclopropane units are typical of this type of structure. The coupling constants in aziridine rings are close to those reported in the literature ($J_{trans} \approx$ 3 Hz)[20].

We have also established a rule to assign the chemical shifts to the appropriate protons in the aziridine rings, which usually appear as doublets; e.g. 1b-H and 2-H (**C**). Diagnostic δ values have been determined for some substituted derivatives. For example, in **49** where 1b-H is replaced by the methyl group, δ(2-H) = 3.32; in **15** for the same situation (1a-H is replaced by the methyl group, N-atom instead of C-7b) δ(1-H) = 3.31. Downfield shift of the 1-H signal (δ = 3.83) in **16** is probably the result of the influence of the phenyl substituent at C-1a, because δ(2-H) is still equal to 3.23. So, the chemical shifts of 1- and 2-H of the aziridine rings usually appear at δ = 3.3–3.5.

The chemical shifts of H_α, H_β, and H_γ in the pyridine moieties have been established on the basis of known relationships between the δ values and coupling constants[21].

An interesting aspect of the spectra of bisannulated products of neopentyl sulfonates is that the protons of the methylene group in the neopentyl substituents are diastereotopic and appear as an AB system with coupling constants close to 10 Hz.

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Experimental

^{1}H NMR: Varian EM-360 (60 MHz), Jeol JNM-4H-100 (100 MHz), and Bruker CPX-300 (300 MHz), TMS as internal standard. – MS: Finnigan 8200. – IR: Beckman IR 4240. – Melting points: uncorrected. – TLC analyses: foil plates Merck 60F 254. – Column chromatography: silica gel 100–200 and 230–400 mesh (Merck), $CHCl_3$/acetone (10:1) as eluent. – Starting materials were either commercially available or prepared by known methods: chloromethyl phenyl sulfone (**1**)[22], *N,N*-dimethyl(chloromethane)sulfonamide (**2**)[23], neopentyl chloromethanesulfonate (**3**)[24], *tert*-butyl chloromethyl sulfone (**4**)[25], chloromethanesulfomorpholide (**5**)[26], chloromethyl *p*-tolyl sulfone (**6**)[27], 1-chloroethyl phenyl sulfone (**7**)[28], bromomethyl *p*-tolyl sulfone (**8**)[22], 2-methylquinoxaline (**10**)[29], 2-phenylquinoxaline (**11**)[30], 6-nitroquinoxaline (**18**)[31], quinoxaline *N*-oxide (**19**)[32], 2(1*H*)-quinoxalinone (**24**)[33], 2-chloroquinoxaline (**26**)[34], 2-methoxyquinoxaline (**27**)[35], 1,5-naphthyridine (**30**)[36], 1,6-naphthyridine (**31**)[36], 1,7-naphthyridine (**32**)[37], 1,8-naphthyridine (**33**)[36], 2-methyl-1,8-naphthyridine (**34**)[36], 4-methyl-1,8-naphthyridine (**35**)[36], 2,6-naphthyridine[38], 5-azaquinoxaline (**51**)[39], 3-phenyl-5-azaquinoxaline (**52**)[40], 2,3-diphenyl-5-azaquinoxaline (**53**)[41].

Reactions of α-haloalkane sulfones and sulfonic acid derivatives with heteroarenes were carried out according to the given procedures (below). Some modifications are noted in the corresponding tables.

Method A; KOH/DMSO System: To a stirred suspension of powdered KOH (4.0 g, 70 mmol) in DMSO (15 ml) a solution of a carbanion precursor (**1–8**) (20 mmol; 10 mmol for the reactions of the quinoxalinone **24**) and a heteroarene (10 mmol) in DMSO (5 ml) was added dropwise at room temp. for 4–5 min.The reaction was continued until the analysis of the reaction mixture showed the absence of one of the substrates (20 min – 5 h). The reaction mixture was poured into a diluted solution of HCl in water (3%), and the precipitate formed was filtered or extracted with $CHCl_3$ or AcOEt (2 × 30 ml). The combined organic layers were washed with water (50 ml) and dried with $MgSO_4$. The crude products were purified by crystallization or column chromatography.

Method B; tBuOK/DMF(DMSO) System: To a stirred solution of *t*BuOK (380 mg, 3.4 mmol) in DMF (7 ml) a solution of the carbanion precursor (**1–8**) (2 mmol) and heteroarene (1 mmol) in DMF (3 ml) was added dropwise during 4–5 min. The reaction was continued until the analysis of the reaction mixture showed the

disappearance of one of the substrates (20–30 min). The reaction mixture was poured into a diluted solution of HCl in water (3%), and treated as in method A.

Method C; KOH/DMF System: Reactions were carried out in analogy to procedure A at 0°C.

Method D; tBuOK/NH$_3$ System: As described earlier[10].

1,1a,1b,2-Tetrahydro-1,2-bis(phenylsulfonyl)bisazirino[1,2-a:2',1'-c]quinoxaline (**12**): M.p. 218°C (AcOH, dec.). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.06–7.45 (m, 10H), 6.92–6.75 (m, 2H), 6.59–6.41 (m, 2H), 3.64 (d, *J* = 2.7 Hz, 2H, 1a-, 1b-H), 3.43 (d, *J* = 2.7 Hz, 2H, 1-, 2-H).

$C_{22}H_{18}N_2O_4S_2$ (438.5)
Calcd. C 60.26 H 4.14 N 6.39 S 14.62
Found C 60.00 H 4.18 N 6.32 S 14.60

1,2-Bis(N,N-dimethylsulfamoyl)-1,1a,1b,2-tetrahydrobisazirino[1,2-a:2',1'-c]quinoxaline (**13**): M.p. 220°C (AcOH, dec.). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 7.40–7.10 (m, 4H), 3.54–3.34 (m, 4H), 3.10 [s, 12H, 2 × $N(CH_3)_2$].

$C_{14}H_{20}N_4O_4S_2$ (372.5)
Calcd. C 45.15 H 5.41 N 15.04 S 17.22
Found C 45.10 H 5.49 N 14.89 S 17.04

1,1a,1b,2-Tetrahydro-1,2-bis(4-morpholinosulfonyl)bisazirino[1,2-a:2',1'-c]quinoxaline (**14**): M.p. 228°C (AcOH, dec.). – ^{1}H NMR (CF_3CO_2H, 100 MHz): δ = 7.58–7.23 (m, 4H), 3.94–3.70 (m, 12H), 3.60–3.40 (m, 8H).

$C_{18}H_{24}N_4O_6S_2$ (456.5)
Calcd. C 47.36 H 5.30 N 12.27 S 14.05
Found C 47.40 H 5.23 N 12.22 S 14.04

1,1a,1b,2-Tetrahydro-1a-methyl-1,2-bis(phenylsulfonyl)bisazirino[1,2-a:2',1'-c]quinoxaline (**15**): M.p. 211–212°C (AcOH). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.23–7.65 (m, 10H), 7.02–6.50 (m, 4H), 3.79 (d, *J* = 2.9 Hz, 1H, 1b-H), 3.33 (d, *J* = 2.9 Hz, 1H, 2-H), 3.31 (s, 1H, 1-H), 2.00 (s, 3H, CH_3).

$C_{23}H_{20}N_2O_4S_2$ (452.5) Calcd. C 61.04 H 4.45 N 6.19
Found C 61.09 H 4.35 N 6.22

1,1a,1b,2-Tetrahydro-1a-phenyl-1,2-bis(phenylsulfonyl)bisazirino[1,2-a:2',1'-c]quinoxaline (**16**): M.p. 185–186°C (AcOH). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 7.60–6.65 (m, 19H), 4.03 (d, *J* = 3.4 Hz, 1H, 1b-H), 3.83 (s, 1H, 1-H), 3.23 (d, *J* = 3.4 Hz, 1H, 2-H).

$C_{28}H_{22}N_2O_4S_2$ (514.6)
Calcd. C 65.35 H 4.31 N 5.44 S 12.46
Found C 65.20 H 4.35 N 5.41 S 12.87

1,2-Bis(N,N-dimethylsulfamoyl)-1,1a,1b,2-tetrahydro-1a-phenylbisazirino[1,2-a:2',1'-c]quinoxaline (**17**): M.p. 202°C (AcOH, dec.). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 7.70–7.20 (m, 9H), 3.94 (d, *J* = 3.2 Hz, 1H, 1b-H), 3.71 (s, 1H, 1-H), 3.10 (d, *J* = 3.2 Hz, 1H, 2-H), 2.69 and 2.59 [2 × s, 12H, 2 × $N(CH_3)_2$].

$C_{20}H_{24}N_4O_4S_2$ (448.6)
Calcd. C 53.55 H 5.39 N 12.49 S 14.29
Found C 53.50 H 5.40 N 12.56 S 14.50

6-Nitro-2-[(p-tolylsulfonyl)methyl]quinoxaline (**20**): M. p. 234–236°C (EtOH/H_2O). – ^{1}H NMR (CF_3CO_2H, 60 MHz): δ = 9.63 (s, 1H, 3-H), 9.43 (d, *J* = 2.0 Hz, 1H, 5-H), 9.00 and 8.68 (AB, *J* = 9.4 Hz, 2H, 7- and 8-H), 7.92 and 7.63 (AB, *J* = 8.0 Hz, 4H, H-Tol), 5.43 (s, 2H, CH_2), 2.60 (s, 3H, CH_3).

$C_{16}H_{13}N_3O_4S$ (343.4) Calcd. C 55.97 H 3.82 N 12.24
Found C 55.69 H 3.63 N 11.83

6-Nitro-2-[1-(phenylsulfonyl)ethyl]quinoxaline (**21**): M. p. 185–186°C (EtOH/H_2O). – ^{1}H NMR (CF_3CO_2H, 60 MHz): δ = 9.69 (s, 1H, 3-H), 9.61 (d, *J* = 2.0 Hz, 1H, 5-H), 9.00 and 8.53 (AB, *J* = 10.0 Hz, 2H, 7- and 8-H), 8.25–7.67 (m, 5H), 5.47 (q, *J* = 6.6 Hz, 1H, CH), 2.07 (d, *J* = 6.6 Hz, 3H, CH_3).

$C_{16}H_{13}N_3O_4S$ (343.4) Calcd. C 55.97 H 3.82 N 12.24
Found C 56.13 H 3.56 N 11.96

2-[(Phenylsulfonyl)methyl]quinoxaline N-Oxide (**22**): M. p. 158–159°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ = 9.03 (s, 1H, 3-H), 8.73–7.50 (m, 9H), 5.17 (s, 2H, CH_2). – MS: *m/z* (%) = 301 (3) [M + 1], 300 (3) [$M^{+\cdot}$], 236 (11) [M – SO_2], 219 (7), 159 (100) [M – SO_2Ph], 143 (27) [M – SO_2Ph – O], 129 (68) [M – CH_2SO_2Ph – O], 102 (40), 77 (30), 51 (19).

$C_{15}H_{12}N_2O_3S$ (300.3) Calcd. C 59.99 H 4.03 N 9.33
Found C 59.94 H 4.00 N 9.08

2-[(N,N-Dimethylsulfamoyl)methyl]quinoxaline N-Oxide (**23**): M. p. 127–128°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.91 (s, 1H, 3-H), 8.65–8.50 and 8.28–8.00 (2 × m, 2H), 7.93–7.63 (m, 2H), 4.75 (s, 2H, CH_2), 2.76 [s, 6H, $N(CH_3)_2$].

$C_{11}H_{13}N_3O_3S$ (267.3) Calcd. C 49.43 H 4.90 N 15.72
Found C 49.08 H 4.84 N 15.44

1,1a-Dihydro-1-(phenylsulfonyl)azirino[1,2-a]quinoxalin-2(3H)-one (**25a**): M.p. 234–235°C (AcOH, dec.). – ^{1}H NMR (CF_3CO_2H, 100 MHz): δ = 9.60 (s, 1H, NH), 8.15–7.60 (m, 5H), 7.25–6.85 (m, 4H), 4.05 and 3.93 (2 × d, *J* = 2.6 Hz, 2H, 1-, 1a-H).

$C_{15}H_{12}N_2O_3S$ (300.3)
Calcd. C 59.99 H 4.03 N 9.33 S 10.67
Found C 60.00 H 4.05 N 9.39 S 10.75

1-(N,N-Dimethylsulfamoyl)-1,1a-dihydroazirino[1,2-a]quinoxalin-2(3H)-one (**25b**): M.p. 213°C (AcOH, dec.). – ^{1}H NMR (CF_3CO_2H, 100 MHz): δ = 9.48 (s, 1H, NH), 7.53–6.88 (m, 4H), 3.98–3.91 (m, 2H, 1-, 1a-H), 3.00 [s, 6H, $N(CH_3)_2$].

$C_{11}H_{13}N_3O_3S$ (267.3)
Calcd. C 49.43 H 4.90 N 15.72 S 11.99
Found C 49.00 H 4.73 N 15.58 S 12.28

1,1a-Dihydro-1-(4-morpholinosulfonyl)azirino[1,2-a]quinoxalin-2(3H)-one (**25c**): M.p. 236°C (AcOH, dec.). – ^{1}H NMR (CF_3CO_2H, 100 MHz): δ = 9.30 (s, 1H, NH), 7.25–6.25 (m, 4H), 3.75–3.15 (m, 10H).

$C_{13}H_{15}N_3O_4S$ (309.3)
Calcd. C 50.48 H 4.89 N 13.58 S 10.36
Found C 50.30 H 4.88 N 13.37 S 10.79

2-[Chloro(phenylsulfonyl)methyl]quinoxaline (**28a**): M. p. 142–144°C (MeOH). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 9.50 (s, 1H, 3-H), 8.40–7.38 (m, 9H), 6.20 (s, 1H, CH).

$C_{15}H_{11}ClN_2O_2S$ (318.8) Calcd. C 56.60 H 3.46 N 8.80
Found C 56.48 H 3.34 N 8.86

2-[Chloro(phenylsulfonyl)methylene]-1,1a,2,3-tetrahydro-1-(phenylsulfonyl)azirino[1,2-a]quinoxaline (Mixture of Isomers) (**29a**): ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 8.54 (s, 1H, NH); 8.14–7.63 (m, 10H); 7.15–6.80 (m, 4H); 5.071 (d, *J* = 2.65 Hz), 5.069 (d, *J* = 2.66 Hz), 4.17 (d, *J* = 2.70 Hz), 4.12–4.09 (m), 4.07 (d, *J* = 2.70 Hz), 4.022 (d, *J* = 2.70 Hz), 4.020 (d, *J* = 2.70 Hz) [2H, 1- and 1a-H, protons of isomers; X-ray investigations will be published elsewhere[42]].

$C_{22}H_{17}ClN_2O_4S_2$ (473.0) Calcd. C 55.93 H 3.60 N 5.93
Found C 55.85 H 3.58 N 5.68

2-[Bromo(p-tolylsulfonyl)methylene]-1,1a,2,3-tetrahydro-1-(p-tolylsulfonyl)azirino[1,2-a]quinoxaline (Mixture of Isomers) (**29d**):

^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 9.03 (s, 1H, NH), 7.93–6.70 (m, 12H), 4.84 and 4.55 (2 × d, *J* = 2.7 Hz, major isomer, 70%) and 4.66–4.63 (m) (2H, 1- and 1a-H), 2.42 (s, 6H, 2 × CH_3).

$C_{24}H_{21}BrN_2O_4S_2$ (545.5) Calcd. C 52.85 H 3.88 N 5.14
Found C 52.41 H 4.17 N 5.25

1a,1b,2,7b-Tetrahydro-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]-cyclopropa[c][1,5]naphthyridine (**36**): M.p. 226–229°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.39–8.27 (m, 1H, 6-H), 8.16–8.01 (m, 4H), 7.91–7.64 (m, 6H), 7.14–6.71 (m, 2H, 4-, 5-H), 3.66 (d, *J* = 2.5 Hz, 1H, 1b-H), 3.48 (d, *J* = 2.5 Hz, 1H, 2-H), 3.20–2.83 (m, 3H, 1-, 1a-, 7b-H).

$C_{22}H_{18}N_2O_4S_2$ (438.5) Calcd. C 60.26 H 4.14 N 6.39
Found C 60.25 H 4.11 N 5.93

1,2-Bis(N,N-dimethylsulfamoyl)-1a,1b,2,7b-tetrahydro-1H-azirino[1,2-a]cyclopropa[c][1,5]naphthyridine (**37**): M.p. 205–206°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.37 (dd, *J* = 4.8, 1.6 Hz, 1H, 6-H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H, 4-H), 7.20 (dd, *J* = 8.0, 4.8 Hz, 1H, 5-H), 3.48 (d, *J* = 2.9 Hz, 1H, 1b-H), 3.42 (d, *J* = 2.9 Hz, 1H, 2-H), 3.03 and 2.96 [2 × s, 12H, 2 × $N(CH_3)_2$], 2.85 (dd, *J* = 9.2, 4.3 Hz, 1H), 2.75 (dd, *J* = 9.2, 4.5 Hz, 1H), 2.63 (dd, *J* = 4.5, 4.3 Hz, 1H, 1-H).

$C_{14}H_{20}N_4O_4S_2$ (372.5) Calcd. C 45.15 H 5.41 N 15.04
Found C 45.30 H 5.44 N 14.38

1a,1b,2,7b-Tetrahydro-1,2-bis[(neopentyloxy)sulfonyl]-1H-azirino[1,2-a]cyclopropa[c][1,5]naphthyridine (**38**): M. p. 177–178°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.40 (dd, *J* = 4.8, 1.8 Hz, 1H, 6-H), 7.63 (dd, *J* = 8.0, 1.8 Hz, 1H, 4-H), 7.22 (dd, *J* = 8.0, 4.8 Hz, 1H, 5-H), 4.05 and 4.03 (AB, *J* = 9.1 Hz, 2H, CH_2), 4.03 and 3.98 (AB, *J* = 9.0 Hz, 2H, CH_2), 3.52 and 3.49 (2 × d, *J* = 2.9 Hz, 2H, 1b-, 2-H), 2.97 (dd, *J* = 9.0, 4.6 Hz, 1H), 2.86–2.80 (m, 2H), 1.02 and 1.00 [2 × s, 18H, 2 × $C(CH_3)_3$].

$C_{20}H_{30}N_2O_6S_2$ (458.6) Calcd. C 52.38 H 6.59 N 6.11
Found C 52.23 H 6.67 N 6.28

1a,1b,2,7b-Tetrahydro-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]-cyclopropa[c][1,6]naphthyridine (**39**): M.p. 218–220°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.40 (s, 1H, 7-H), 8.23 (d, *J* = 5.0 Hz, 1H, 5-H), 8.15–8.00 (m, 4H), 7.90–7.60 (m, 6H), 6.35 (d, *J* = 5.0 Hz, 1H, 4-H), 3.65 and 3.55 (2 × d, *J* = 2.8 Hz, 2H, 1b- and 2-H), 2.95–2.78 (m, 3H, 1-, 1a, 7b-H).

$C_{22}H_{18}N_2O_4S_2$ (438.5) Calcd. C 60.26 H 4.14 N 6.39
Found C 60.17 H 4.21 N 5.92

1,2-Bis(N,N-dimethylsulfamoyl)-1a,1b,2,7b-tetrahydro-1H-azirino[1,2-a]cyclopropa[c][1,6]naphthyridine (**40**): M.p. 240–241°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.55 (s, 1H, 7-H), 8.45 (d, *J* = 5.3 Hz, 1H, 5-H), 7.21 (d, *J* = 5.3 Hz, 1H, 4-H), 3.50 and 3.46 (2 × d, *J* = 3.0 Hz, 2H, 1b-, 2-H), 3.05 and 2.95 [2 × s, 12H, 2 × $N(CH_3)_2$], 2.70–2.56 (m, 3H, 1-, 1a-, 7b-H).

$C_{14}H_{20}N_4O_4S_2$ (372.5) Calcd. C 45.15 H 5.41 N 15.04
Found C 45.60 H 5.50 N 15.06

1a,1b,2,7b-Tetrahydro-1,2-bis[(neopentyloxy)sulfonyl]-1H-azirino[1,2-a]cyclopropa[c][1,6]naphthyridine (**41**): M.p. 190–191°C (EtOH). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 8.58 (s, 1H, 7-H), 8.38 (d, *J* = 5.25, 1H, 5-H), 7.19 (d, *J* = 5.25, 1H, 4-H), 4.62 and 3.43 (2 × d, *J* = 2.95 Hz, 2H, 1b-, 2-H), 4.05 and 4.04 (AB, *J* = 9.1 Hz, 2H, CH_2), 4.03 and 4.01 (AB, *J* = 9.2 Hz, 2H, CH_2), 3.70 (dd, *J* = 4.5, 4.3 Hz, 1H, 1-H), 2.78 (dd, *J* = 9.4, 4.3 Hz, 1H), 2.69 (dd, *J* = 9.4, 4.5 Hz, 1H), 0.964 and 0.961 [2 × s, 18H, 2 × $C(CH_3)_3$].

$C_{20}H_{30}N_2O_6S_2$ (458.6) Calcd. C 52.38 H 6.59 N 6.11
Found C 52.14 H 6.69 N 5.97

1a,1b,2,7b-Tetrahydro-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]-cyclopropa[c][1,7]naphthyridine (**42**): M.p. 230–233°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 8.23 (d, *J* = 4.4 Hz, 1H, 6-H), 8.13–7.76 (m, 11H), 7.09 (d, *J* = 4.4 Hz, 1H, 7-H), 3.64 (d, *J* = 2.8 Hz, 1H, 1b-H), 3.48 (d, *J* = 2.8 Hz, 1H, 2-H), 3.00–2.65 (m, 3H, 1-, 1a-, 7b-H).

$C_{22}H_{18}N_2O_4S_2$ (438.5) Calcd. C 60.26 H 4.14 N 6.39
Found C 60.43 H 3.86 N 6.38

1,2-Bis(N,N-dimethylsulfamoyl)-1a,1b,2,7b-tetrahydro-1H-azirino[1,2-a]cyclopropa[c][1,7]naphthyridine (**43**): M.p. 250–251°C (EtOH/H_2O). – ^{1}H NMR (CF_3CO_2H, 300 MHz): δ = 8.49 (s, 1H, 4-H), 8.02 (d, *J* = 6.0 Hz, 1H, 6-H), 7.48 (d, *J* = 6.0 Hz, 1H, 7-H), 3.63 and 3.53 (2 × d, *J* = 3.2 Hz, 2H, 1b- and 2-H), 2.77 and 2.67 [2 × s, 12H, 2 × $N(CH_3)_2$], 2.80–2.60 (m, 3H, 1-, 1a-, 7b-H).

$C_{14}H_{20}N_4O_4S_2$ (372.5) Calcd. C 45.15 H 5.41 N 15.04
Found C 45.44 H 5.55 N 15.31

1a,1b,2,7b-Tetrahydro-1,2-bis[(neopentyloxy)sulfonyl]-1H-azirino[1,2-a]cyclopropa[c][1,7]naphthyridine (**44**): M.p. 190–191°C (EtOH). – ^{1}H NMR (CF_3CO_2H, 300 MHz): δ = 8.48 (s, 1H, 4-H), 8.08 (d, *J* = 6.0 Hz, 1H, 6-H), 7.43 (d, *J* = 6.0 H, 1H, 7-H), 4.02 and 3.99 (AB, *J* = 9.8 Hz, 2H, CH_2), 3.91 and 3.90 (AB, *J* = 8.6 Hz, 2H, CH_2), 3.55 and 3.53 (AB, *J* = 3.1 Hz, 2H, 1b-, 2-H), 2.85 (dd, *J* = 4.7, 4.5 Hz, 1H, 1-H), 2.75 (dd, *J* = 8.7, 4.5 Hz, 1H), 2.60 (dd, *J* = 8.7, 4.7 Hz, 1H), 0.88 [s, 18H, 2 × $C(CH_3)_3$].

$C_{20}H_{30}N_2O_6S_2$ (458.6) Calcd. C 52.38 H 6.59 N 6.11
Found C 52.25 H 6.71 N 6.19

1a,1b,2,7b-Tetrahydro-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]-cyclopropa[c][1,8]naphthyridine (**45**): M.p. 228–231°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.14–7.00 (m, 13H), 3.55 and 3.54 (AB, *J* = 2.9 Hz, 2H, 1b-, 2-H), 2.87–2.62 (m, 3H, 1-, 1a-, 7b-H).

$C_{22}H_{18}N_2O_4S_2$ (438.5) Calcd. C 60.26 H 4.14 N 6.39
Found C 60.32 H 4.02 N 5.96

1,2-Bis(N,N-dimethylsulfamoyl)-1a,1b,2,7b-tetrahydro-1H-azirino[1,2-a]cyclopropa[c][1,8]naphthyridine (**46**): M.p. 221–222°C (EtOH/H_2O). – ^{1}H NMR ([D$_6$]DMSO, 100 MHz): δ = 8.55–8.40 (m, 1H, 5-H), 8.09–7.91 (m, 1H, 7-H), 7.43–7.23 (m, 1H, 6-H), 4.38 and 3.53 (2 × d, *J* = 2.8 Hz, 2H, 1b-, 2-H), 3.68–3.18 (m, 3H, 1-, 1a-, 7b-H), 3.08 and 2.94 [2 × s, 12H, 2 × $N(CH_3)_2$].

$C_{14}H_{20}N_4O_4S_2$ (372.5) Calcd. C 45.15 H 5.41 N 15.04
Found C 45.24 H 5.44 N 15.02

1a,1b,2,7b-Tetrahydro-1,2-bis[(neopentyloxy)sulfonyl]-1H-azirino[1,2-a]cyclopropa[c][1,8]naphthyridine (**47**): M.p. 298°C (EtOH/H_2O, dec.). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.37 (dd, *J* = 4.8, 1.8 Hz, 1H, 5-H), 7.68 (dd, *J* = 7.6, 1.8 Hz, 1H, 7-H), 7.16 (dd, *J* = 7.6, 4.8 Hz, 1H, 6-H), 4.68 (d, *J* = 9.2 Hz, 1H of CH_2), 4.18 (d, *J* = 9.2 Hz, 1H of CH_2), 3.96 and 3.95 (AB, *J* = 9.0 Hz, 2H, CH_2), 3.63 and 3.61 (AB, *J* = 2.9 Hz, 2H, 1b-, 2-H), 2.83, 2.75 and 2.69 (ABX, $|J_{AB}|$ = 7.7, J_{AX} = −4.3, J_{BX} = −4.5 Hz, 3H, 1-, 1a-, 7b-H), 1.02 [s, 18H, 2 × $C(CH_3)_3$].

$C_{20}H_{30}N_2O_6S_2$ (458.6) Calcd. C 52.38 H 6.59 N 6.11
Found C 52.24 H 6.68 N 5.92

1a,1b,2,7b-Tetrahydro-5-methyl-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]cyclopropa[c][1,8]naphthyridine (**48**): M.p. 221–223°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13–7.91 (m, 4H), 7.73–7.56 (m, 6H), 7.35 (d, *J* = 7.7 Hz, 1H, 7-H), 6.84 (d, *J* = 7.7 Hz, 1H, 6-H), 3.58 (d, *J* = 2.8 Hz, 1H, 1b-H), 3.45 (d, *J* = 2.8 Hz, 1H, 2-H), 2.83–2.57 (m, 3H, 1-, 1a-, 7b-H), 2.26 (s, 3H, CH_3).

$C_{23}H_{20}N_2O_4S_2$ (452.5) Calcd. C 61.04 H 4.45 N 6.19
Found C 61.17 H 4.34 N 5.87

1a,1b,2,7b-Tetrahydro-1b-methyl-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]cyclopropa[c][1,8]naphthyridine (**49**): M. p. 248–249°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.17 (dd, *J* = 4.9, 1.8 Hz, 1H, 5-H), 8.08–7.90 (m, 4H), 7.71–7.50 (m, 7H), 7.00 (dd, *J* = 7.7, 4.9 Hz, 1H, 6-H), 3.32 (s, 1H, 2-H), 2.94–2.90 (m, 1H), 2.66–2.57 (m, 2H), 1.51 (s, 3H, CH_3).

$C_{23}H_{20}N_2O_4S_2$ (452.5) Calcd. C 61.04 H 4.45 N 6.19
Found C 60.78 H 4.36 N 5.78

1a,1b,2,7b-Tetrahydro-7-methyl-1,2-bis(phenylsulfonyl)-1H-azirino[1,2-a]cyclopropa[c][1,8]naphthyridine (**50**): M.p. 220–223°C (EtOH/H_2O). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.09–8.07 (m, 2H), 7.97 (d, *J* = 4.3 Hz, 1H, 5-H), 7.95–7.92 (m, 2H), 7.74–7.55 (m, 6H), 6.83 (d, *J* = 4.3 Hz, 1H, 6-H), 3.55–3.53 (m, 2H, 1b-, 2-H), 2.81–2.63 (m, 3H, 1-, 1a-, 7b-H), 2.17 (s, 3H, CH_3).

$C_{23}H_{20}N_2O_4S_2$ (452.5) Calcd. C 61.04 H 4.45 N 6.19
Found C 61.12 H 4.34 N 5.96

3-Phenyl-8-[(p-tolylsulfonyl)methyl]pyrido[2,3-b]pyrazine (**54**): M.p. 228–230°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.17 (d, *J* = 4.41 Hz, 1H, 6-H), 9.16 (s, 1H, 2-H), 7.76 (d, *J* = 4.41 Hz, 1H, 7-H), 8.29–8.26 and 7.60–7.10 (2 × m, 9H), 5.17 (s, 2H, CH_2), 2.29 (s, 3H, CH_3). – IR ($CHCl_3$): $\tilde{\nu}$ = 1315 cm^{-1}, 1150, 1080. – MS: *m/z* (%) = 375 (0.4) [$M^{+\cdot}$], 312 (28), 311 (100) [M – SO_2], 310 (53) [M – HSO_2], 296 (15) [M – SO_2 – CH_3], 220 (58) [M – SO_2Tol], 193 (11) [M – SO_2Tol – HCN], 91 (40) [$C_7H_7^+$], 77 (10), 65 (18), 63 (21), 51 (8), 43 (9).

$C_{21}H_{17}N_3O_2S$ (375.4)
Calcd. C 67.18 H 4.56 N 11.19 S 8.54
Found C 66.80 H 4.28 N 10.85 S 8.39

2,3-Diphenyl-8-[(phenylsulfonyl)methyl]pyrido[2,3-b]pyrazine (**55**): M.p. 188–189°C (EtOH). – ^{1}H NMR ([D_6]acetone, 60 MHz): δ = 8.83 (d, *J* = 8.5 Hz, 1H, 6-H), 7.90 (d, *J* = 8.5 Hz, 1H, 7-H), 7.76–7.13 (m, 15H), 5.30 (s, 2H, CH_2). – MS: *m/z* (%) = 437 (49) [$M^{+\cdot}$], 373 (12) [M – SO_2], 297 (28), 296 (100) [M – SO_2Ph], 295 (18), 283 (7), 193 (29), [M – SO_2Ph – PhCN], 166 (14), 125 (16), 111 (13), 97 (34), 83 (33), 77 (14), 71 (39), 57 (55).

$C_{26}H_{19}N_3O_2S$ Calcd. 437.1198 Found 437.1198 (HR-MS)

1,2-Bis(tert-butylsulfonyl)-1,1a,1b,2-tetrahydrobisazirino[1,2-a:2',1'-c]pyrido[2,3-e]pyrazine (**56**): M.p. 231–233°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.30 (dd, *J* = 4.6, 1.7 Hz, 1H, 5-H), 7.74 (dd, *J* = 7.7, 1.7 Hz, 1H, 7-H), 7.17 (dd, *J* = 7.7, 4.6 Hz, 1H, 6-H), 3.79, 3.69 and 3.61, 3.54 (2 × AB, *J* = 2.9 Hz, 4H, 1-, 1a-, 1b-, 2-H), 1.61 and 1.52 [2 × s, 18H, 2 × $C(CH_3)_3$]. – IR ($CHCl_3$): $\tilde{\nu}$ = 1305 cm^{-1}, 1150, 1120. – MS: *m/z* (%) = 399 (1) [$M^{+\cdot}$], 278 (25) [M – SO_2tBu], 222 (6), 206 (2), 174 (28), 158 (100) [M – 2 × SO_2tBu + 1], 145 (12), 131 (13), 104 (6), 57 (69) [tBu$^+$], 41 (28).

$C_{17}H_{25}N_3O_4S_2$ (399.5)
Calcd. C 51.11 H 6.31 N 10.52 S 16.05
Found C 50.99 H 6.33 N 10.25 S 15.48

1,1a,1b,2-Tetrahydro-1,2-bis(p-tolylsulfonyl)bisazirino[1,2-a:2',1'-c]pyrido[2,3-e]pyrazine (**57**): M.p. 229–230°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.00–7.40 (m, 8H), 8.07, 6.98, 6.90 (ABX, $|J_{AB}|$ = 7.7, J_{AX} = –4.9, J_{BX} = –1.8 Hz, 3H, 5-, 6-, 7-H), 3.67, 3.58 and 3.59, 3.50 (2 × AB, *J* = 2.9 Hz, 4H, 1-, 1a-, 1b-, 2-H), 2.50 and 2.47 (2 × s, 6H, 2 × CH_3). – IR ($CHCl_3$): $\tilde{\nu}$ = 1320 cm^{-1}, 1145, 1080. – MS: *m/z* (%) = 467 (2) [$M^{+\cdot}$], 312 (35) [M – SO_2Tol], 173 (4) [M – SO_2Tol-SOTol], 156 (16), 146 (16), 139 (100) [TolSO$^+$], 123 (21), 119 (12), 91 (68) [$C_7H_7^+$], 77 (13), 65 (26), 45 (11). $C_{23}H_{21}N_3O_4S_2$ (467.6)
Calcd. C 59.08 H 4.53 N 8.99 S 13.71
Found C 58.74 H 4.55 N 8.54 S 13.41

1,1a,1b,2-Tetrahydro-1b-phenyl-1,2-bis(p-tolylsulfonyl)bisazirino[1,2-a:2',1'-c]pyrido[2,3-e]pyrazine (**58**): M.p. 223–224°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.16–7.02 (m, 16H), 3.96 (d, *J* = 2.9 Hz, 1H, 1a-H), 3.81 (s, 1H, 2-H), 3.10 (d, *J* = 2.9 Hz, 1H, 1-H), 2.44 and 2.38 (2 × s, 6H, 2 × CH_3). – MS: *m/z* (%) = 543 (0.2) [$M^{+\cdot}$], 388 (11) [M – SO_2Tol], 246 (7), 234 (15), 233 (41) [M – 2 × SO_2Tol], 232 (71), 221 (73), 194 (19), 155 (14) [TolSO$_2^+$], 139 (63) [TolSO$^+$], 123 (25), [TolS$^+$], 91 (100) [$C_7H_7^+$], 77 (31), 65 (44), 51 (18), 45 (13), 39 (36).

$C_{29}H_{25}N_3O_4S_2$ (543.7)
Calcd. C 64.07 H 4.64 N 7.73 S 11.79
Found C 63.70 H 4.64 N 7.41 S 11.45

1a,1b,2,7b-Tetrahydro-5-phenyl-1,2-bis(p-tolylsulfonyl)-1H-azirino[1',2':1,6]cyclopropa[4,5]pyrido[2,3-b]pyrazine (**59**): M.p. 297–300°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.68 (s, 1H, 6-H), 8.00–7.40 (m, 13H), 3.73 and 3.60 (2 × d, *J* = 2.9 Hz, 2H, 1b-, 2-H), 3.15–2.80 (m, 3H, 1-, 1a-, 7b-H), 2.49 and 2.48 (2 × s, 6H, 2 × CH_3). – IR (KBr): $\tilde{\nu}$ = 1310 cm^{-1}, 1300, 1145, 1080. – MS: *m/z* (%) = 543 (0.9) [$M^{+\cdot}$], 388 (93) [M – SO_2Tol], 246 (13), 234 (24), 233 (42) [M – 2 × SO_2Tol], 232 (49), 221 (77), 194 (9), 156 (15) [M – 2 × SO_2Tol – Ph], 139 (46) [TolSO$^+$], 123 (22) [TolS$^+$], 92 (36), 91 (100) [$C_7H_7^+$], 77 (32), 65 (39), 51 (14), 44 (34).

$C_{29}H_{25}N_3O_4S_2$ (543.7)
Calcd. C 64.07 H 4.64 N 7.73 S 11.79
Found C 63.78 H 4.43 N 7.27 S 11.48

1a,1b,2,7b-Tetrahydro-5,6-diphenyl-1,2-bis(phenylsulfonyl)-1H-azirino[1',2':1,6]cyclopropa[4,5]pyrido[2,3-b]pyrazine (**60**): M.p. 273–275°C ($CHCl_3$/acetone). – ^{1}H NMR ($CDCl_3$/[D_6]acetone, 60 MHz): δ = 8.28–6.94 (m, 20H), 4.17 (d, *J* = 3.0 Hz, 1H, 1b-H), 3.64 (d, *J* = 3.0 Hz, 1H, 2-H), 3.61–3.40 (m, 1H, 1-H), 3.11–2.74 (m, 2H, 1a-, 7b-H). – MS: *m/z* (%) = 591 (13) [$M^{+\cdot}$], 451 (40), 450 (89) [M – SO_2Ph], 386 (6) [M – SO_2Ph – SO_2], 309 (52) [M – 2 × SO_2Ph], 308 (54), 297 (55), 282 (17) [M – 2 × SO_2Ph – HCN], 281 (17), 256 (10), 236 (13), 179 (11), 152 (10), 137 (10), 129 (16), 125 (16), 111 (24), 105 (100), 97 (40), 83 (37), 77 (49) [$C_6H_5^+$], 69 (46), 43 (37).

$C_{33}H_{25}N_3O_4S_2$ (591.7)
Calcd. C 66.99 H 4.26 N 7.10 S 10.84
Found C 66.85 H 4.16 N 7.07 S 10.80

3-[(p-Tolylsulfonyl)methyl]pyrido[2,3-b]pyrazine (**61**): M.p. 171–172°C (EtOH). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.16 (s, 1H, 2-H), 9.14 (dd, *J* = 4.4, 1.8 Hz, 1H, 6-H), 8.50 (dd, *J* = 8.4, 1.8 Hz, 1H, 8-H), 7.75 (dd, *J* = 8.4, 4.4 Hz, 1H, 7-H), 7.57 and 7.24 (2 × d, *J* = 8.3 Hz, 4H, H-Tol), 4.88 (s, 2H, CH_2), 2.38 (s, 3H, CH_3). – MS: *m/z* (%) = 299 (2) [$M^{+\cdot}$], 235 (76) [M – SO_2], 234 (100) [M – HSO_2], 221 (12), 220 (70), 219 (13), 144 (24) [M – SO_2Tol], 103 (43), 91 (40) [$C_7H_7^+$], 77 (9), 65 (11), 63 (8).

$C_{15}H_{13}N_3O_2S$ (299.3)
Calcd. C 60.19 H 4.38 N 14.04 S 10.71
Found C 59.80 H 4.25 N 14.19 S 10.50

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1: 7205-98-3 / **2**: 35427-68-0 / **3**: 86434-24-4 / **4**: 24824-96-2 / **5**: 39542-27-3 / **6**: 7569-26-8 / **7**: 13557-25-0 / **8**: 37891-95-5 / **9**: 91-19-0 / **10**: 7251-61-8 / **11**: 5021-43-2 / **12**: 130008-11-6 / **13**: 130008-12-7 / **14**: 130008-13-8 / **15**: 129919-31-9 / **16**: 130008-14-9 / **17**: 130008-15-0 / **18**: 6639-87-8 / **19**: 6935-29-1 / **20**: 109297-27-0 / **21**: 129919-32-0 / **22**: 109297-26-9 / **23**: 129919-33-1 / **24**: 1196-57-2 / **25a**: 129919-50-2 / **25b**: 129919-51-3 / **25c**: 129919-52-4 / **26**: 1448-87-9 / **27**: 39209-88-6 / **28a**: 129919-53-5 / **29a**: 129919-54-6 / **29d**: 129919-55-7 / **30**: 254-79-5 / **31**: 253-72-5 / **32**: 253-69-0 / **33**: 254-60-4 / **34**: 1569-16-0 / **35**: 1569-17-1 / **36**: 130008-16-1 / **37**: 130008-17-2 / **38**: 129919-34-2 / **39**: 130008-18-3 / **40**: 129919-35-3 / **41**:

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[241/90]