ACID CATALYZED REACTIONS OF 2-VINYLANILINE DERIVATIVES WITH CYCLIC KETONES OF THE TETRALONE-, CHROMAN-4-ONE- AND 2,3-DIHYDRO-1*H*-QUINOLIN-4-ONE SERIES. *N(O)*-HETEROCYCLES VIA 6Π ELECTROCYCLIC REARRANGEMENTS OR [1,5] DIPOLAR ELECTROCYCLIZATIONS. PART 3[1]

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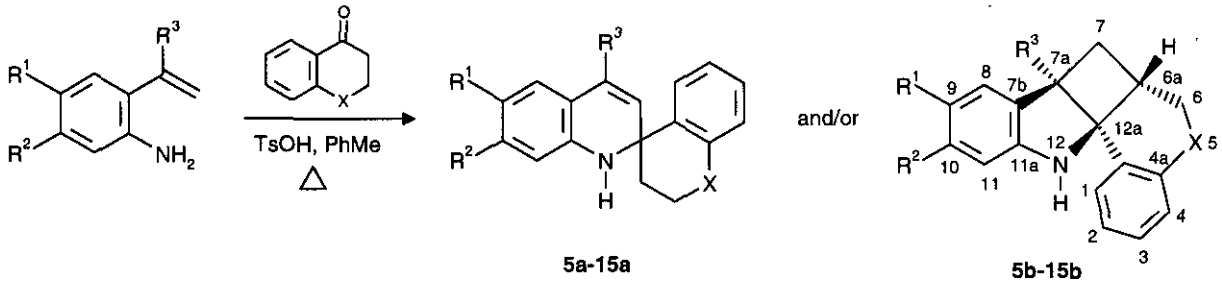
Abstract - The reaction of several 2-vinylaniline derivatives with α-tetralone, chroman-4-one and 2,3-dihydro-1-methyl-1*H*-quinolin-4-one at temperatures between 110 and 115°C with toluene-4-sulfonic acid as catalyst was studied. A series of polycyclic cyclobut[1,2-*b*]indoles, cyclobut[1,2-*c*]chromans, cyclobut[1,2-*c*]quinolines and spirocyclic 1*H*(1'*H*)quinolines was obtained in moderate to very good yields. Mechanistical details as well as scope and limitations of the new method are discussed.

The utility of 2-vinylaniline derivatives in the synthesis of *N*-heterocycles such as quinolines,[2-4] 1,2-dihydro-4-phenylquinolines,[1] quinolin-2-ones,[5] cinnolines[6-8] and octahydropyrido[4',3':1,4]cyclobut[1,2-*b*]-indoles[9] is well documented. Recently we have shown that the toluenesulfonic acid catalyzed reaction of 2-vinylaniline derivatives with acylated aromatic and heterocyclic compounds led to 1,2-dihydroquinolines or cyclobut[*b*]indoles or mixtures of 1,2-dihydroquinolines and cyclobut[*b*]indoles.[1] It could be concluded from these results that the selectivity strongly depends on the structure of the amines and ketones used. Additionally we have shown that when cyclic ketones such as *N*-benzylpiperidin-4-one and *N*-

methylpiperidin-4-one are used in this reaction, octahydropyrido[4',3':1,4]cyclobut[1,2-*b*]indoles were isolated in good yields.[9] This observation demonstrated that the acid catalyzed reaction of 2-vinylaniline derivatives with cyclic ketones is useful for the synthesis of new complex *N*-heterocycles such as polycyclic indole derivatives. In the light of this result further investigations with cyclic ketones were considered to be of potential for the synthesis of various heterocyclic compounds. In a first exploratory phase, we have chosen α-tetralone, chroman-4-one and 2,3-dihydro-1-methyl-1*H*-quinolin-4-one as model ketones and we report here on our first major results in the acid catalyzed reaction of several 2-(1-phenylvinyl)anilines and 2-isopropenylanilines with these ketones (Scheme 1, Table 1).

Scheme 1



5a-15a
(racemic)

5b-15b
(racemic)

1 (R^1=R^2=H, R^3=Me)

2 (R^1=H, R^2=Cl, R^3=Me)

3 (R^1=R^2=H, R^3=Ph)

4 (R^1=Cl, R^2=H, R^3=Ph)

X=CH_2, O, NMe

Table 1 Acid Catalyzed Reactions of 2-Vinylaniline-Derivatives with Cyclic Ketones[a]

R^1	R^2	R^3	X	Reaction time [h]	Product	Yield [%]
H	H	Me	CH_2	15	5b	88
H	Cl	Me	CH_2	15	6b	50 (68[b])
H	H	Ph	CH_2	12	7a	86
Cl	H	Ph	CH_2	15	8a	60
H	H	Me	O	15	9b	20
H	Cl	Me	O	18	10b	27 (50[b])
H	H	Ph	O	15	11a	22
Cl	H	Ph	O	18	12a	74
H	H	Me	NMe	18	13b	54
H	Cl	Me	NMe	18	14b	43
H	H	Ph	NMe	15	15b	23 (43[b])

[a] The reaction conditions are not optimized. In all cases, TsOH was used as catalyst and the reaction carried out in refluxing toluene.

[b] Crude yield (determined by nmr spectroscopy). Yields are low due to isolation problems.

RESULTS AND DISCUSSION

For the acid catalyzed reaction of 2-vinylanilines (**1-4**) with α-tetralone, a general prediction of the expected products seemed to be difficult, because the selectivity in the reaction of 2-vinylaniline derivatives with acetophenones was shown to depend strongly on the structure of the starting anilines.[1] In that case, only anilines (**3**) and (**4**) showed good selectivity and therefore only the reaction of 2-(1-phenylvinyl)anilines with α-tetralone was expected to show good selectivity, too. This turned out to be

indeed the case and the spirocyclic 1*H*-quinolines (**7a**) and (**8a**) were obtained in good to very good yields, unaccompanied by any byproducts arising from the '[1,5] dipole route' (steps ④, ⑥ and ⑦ in Scheme 3). A completely different situation arose, when the 2-isopropenylanilines (**1**) and (**2**) were used in the same reaction. In these cases the polycyclic indole derivatives (**5b**) and (**6b**) were obtained as major products in preparatively useful yields. As nmr spectroscopic studies clearly show (see spectroscopic part) the compounds (**5b**) and (**6b**) are diastereomerically pure and we think that this is the result of a high diastereoselective reaction process (see mechanistic details) and not a loss of other possible diastereoisomers during work-up. As a major byproduct in the reaction with aniline (**2**), the spirocyclic 1*H*-quinoline (**6a**) was isolated (~25-30%), indicating, that in this case the '6π route' (steps ② and ③ in Scheme 3) competes with the '[1,5] dipole route'.[1,9]

The reactions of anilines (**1-4**) with chroman-4-one were similar to that with α-tetralone. Generally the yields were much lower than those obtained with α-tetralone. The best yield (74%) was obtained, when 4-chloro-2-(1-phenylvinyl)aniline (**4**) was used. Table 1 shows, that the reaction of anilines (**3**) and (**4**) with chroman-4-one yielded spirocyclic 1'*H*-quinolines (**11a**) and (**12a**) in moderate to good yields, accompanied by several unidentified byproducts. From the 2-isopropenylanilines (**1**) and (**2**) the cyclobut[1,2-*c*]chromans were obtained in diastereomerically pure form in poor isolated yields of 20 and 27% respectively. In both cases material was lost during flash chromatography and crystallization, necessary for the purification. From the reaction with **2** the spiro[chroman-4,2'(1'*H*)quinoline] (**10a**) was isolated in 20% yield, which showed again the competition of the '[1,5] dipole route' with the '6π route'. A similar product was observed in the reaction with (**1**).

The reactions of the anilines (**1-4**) with 2,3-dihydro-1-methylquinolin-4-one were expected to take place exclusively *via* the '[1,5] dipole route' in analogy with the corresponding reactions of *N*-substituted piperidin-4-ones.[9] Indeed, in all experiments, no products arising from the '6π route' were detected and the cyclobut[1,2-*c*]quinolines (**13b-15b**) were obtained diastereomerically pure in yields of 40 to 50%. The yields were lower than those from the reaction of 2-vinylanilines with *N*-substituted piperidin-4-one derivatives due to the formation of quinolinium *p*-toluenesulfonates (**19-21**) as byproducts. Even under an atmosphere of nitrogen the formation of the quinolinium salts (**19-21**) could not be suppressed. The yields in all the reactions discussed above are unoptimized.

SPECTROSCOPIC PART

The three types of chemical classes were distinguished mainly by nmr spectroscopy. In some cases the assignment of the ^{1}H- and ^{13}C-nmr-signals were confirmed by 2D nmr (COSY, HSQC[10], HMBC[11]). The stereochemistry of the cyclobutane compounds (**5b, 6b, 9b, 10b** and **13b-15b**) was assigned on the basis of 1D ^{1}H-NOE difference spectroscopy (Figure 1). All NOE spectra of the cyclobutane compounds show qualitatively the same dipolar interaction and are summarized in Table 2. The integrals of the NOE effects were calibrated within one molecule with the NOE between the geminal C-7-protons and divided into three categories: strong (s), medium (m) and weak (w).

Figure 1

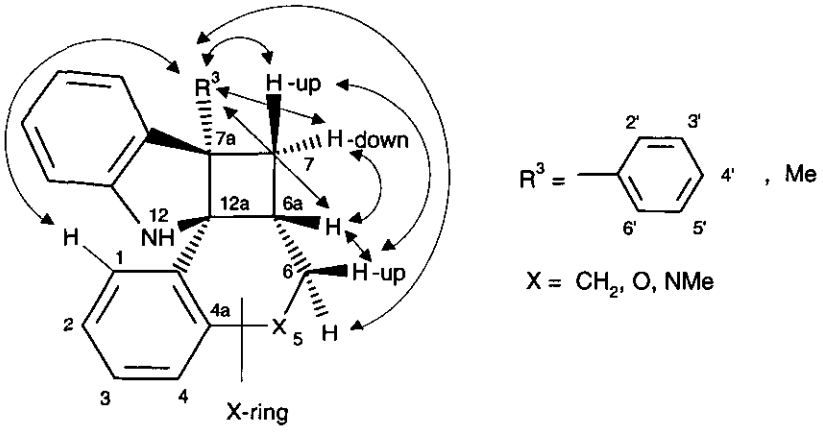


Table 2 Relevant NOE's for all compounds of the b-series (cyclobutanes)

Compound	NOE					
	7a-Me/ H-1	7a-Me/ H-7-down	7a-Me/ H-7-up	H-6a/ H-7-up	H-6a/ H-7-down	7a-Me/ H-6a
5b	m	m	0	#	#	0
6b	m	m	0	#	#	0
9b	m	m	0	m	0	0
10b	m	m	0	m	0	0
13b	w	m	0	m	0	0
14b	w	m	0	#	0	0

Compound	NOE		
15b*	H-2'/6' / H-1	H-2'/6' / H-6-down	H-6a / H-6-up
	m	s	m

= signal overlapping (NOE not detectable)

* NOE experiment in benzene - d_6

H-10-up: low field signal of H-10; H-10-down: high field signal of H-10

s: strong NOE; m: medium NOE; w: weak NOE; 0: no NOE

A positive NOE between C-7a-Me and H-1 in compounds (**5b, 6b, 9b, 10b, 13b** and **14b**) and between the ortho-protons of the phenyl group (H-2'/H-6') and H-1 in compound (**15b**) is a direct proof for the cis-configuration of the dihydroindole ring at the C-12a- and C-7a centers. An observed NOE between H-2'/H-6' and H-6-down in the case of compound (**15b**) indicates that the X-ring (definition see Figure 1) also has a cis configuration at C-12a and C-6a. Cis-configuration of the X-ring of the compounds (**5b, 6b, 9b, 10b, 13b** and **14b**) can only be proved indirectly *via* H-6a and H-7. NOE's between C-7a-Me / H-7-

down are larger than NOE's between C-7a-Me / H-7-up, NOE's between H-6a / H-7-up are larger than NOE's between H-6a / H-7-down and there are no NOE's between C-7a-Me / H-6a. In summary the NOE investigations clearly indicate the cis-configuration as well as for the dihydroindole ring as the X-ring and therefore both ring systems are on different sites of the cyclobutane ring.

MECHANISTIC ASPECTS

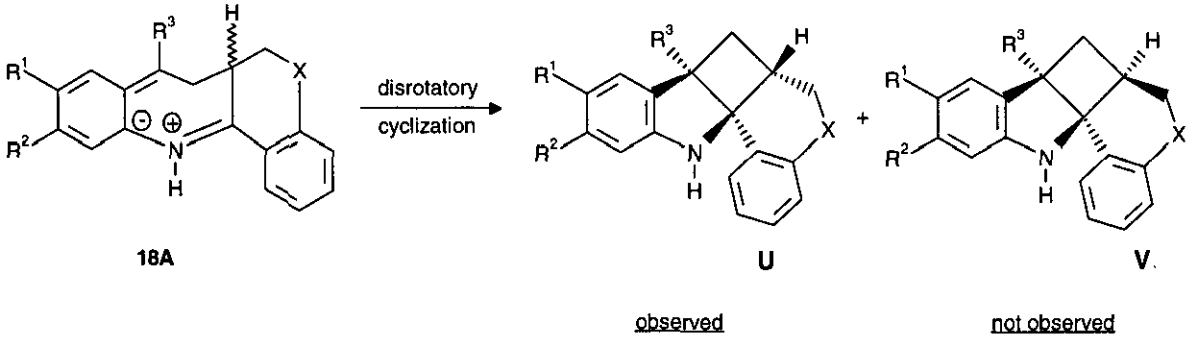
As we can see from Scheme 2, step ① (anil formation) in the reaction sequence is common for all cyclic ketones. In all cases this step required the presence of acid. The acid catalyzed tautomerization (step ④ in Scheme 3) to the enamines (**17**), cyclization to the azomethineylid intermediate (**18**) (step ⑥ in Scheme 3) and subsequent intramolecular [1,5] dipolar cyclization (step ⑦ in Scheme 3) leads to polycyclic cyclobut[1,2-*b*]indoles (**5b-8b**), cyclobut[1,2-*c*]chromans (**10b-12b**) and the cyclobut[1,2-*c*]quinolines (**13b-15b**) (≡'[1,5] dipole route'). The observed diastereoselective formation of these polycyclic compounds is interesting. We think, that the stereochemistry in the '[1,5] dipole route' is mainly determined by the [1,5] dipolar cyclization step. In the literature a few diastereoselective [1,5] electrocyclizations are described.[12,13] In our case, we assume that the seven membered ring in the dipolar structure (**18**) has a *cis*-configuration (the existence of a trans-configuration is unlikely due to steric strain!) and we can apply the Woodward-Hoffmann rules[14,15] to the cyclization of the 1,5 dipole (**18A**). These rules only allow a thermal disrotatory cyclization process, which should lead to two diastereomeric polycyclic systems (**U**) and (**V**) (Scheme 2). However, only one diastereoisomer, namely (**U**) is formed. Studying molecular models, the isomer (**V**) turns out to be a highly strained molecule (the C-6a-C-12a-bond in the cyclobutane ring is twisted!). We assume that this steric strain is still present in the transition state leading to diastereoisomer (**V**). Therefore, we think, the diastereoisomer (**V**) is not observed as a reaction product. For a more complete discussion of mechanistic details, concerning the formation of the cyclobutane derivatives, we should also take into account a possible cyclization of the enamines (**17**), leading to the aziridines (**22**) (step ⑨ in Scheme 3), which can either form the 1,5 dipolar species (**18**) by thermally induced conrotatory ring opening of the aziridine ring (step ⑧ in Scheme 3)[16,17] and then follow the [1,5] electrocyclization pathway, or directly give the cyclobutane derivatives of the b-series by a

thermal [1,3] sigmatropic rearrangement (step ⑩ in Scheme 3).[13b,18,19] Due to steric reasons, we think, we can assume a cis-configuration for the aziridine ring in **22**. Studying molecular models of **22**, we can exclude an orbital symmetry allowed thermal antarafacial [1,3] rearrangement due to geometric reasons.[20] Furthermore our studies clearly show that an allowed thermal suprafacial [1,3] rearrangement leads to the wrong stereochemistry at C-12a and can therefore being excluded too. The only possibility for the formation of the cyclobutane derivatives by thermal [1,3] rearrangement, starting from the aziridine (**22**), are orbital symmetry forbidden processes, which have been discussed in the literature in some cases.[21] In summary, we think that the formation of the 1,5 dipolar species (**18**) is either possible by cyclization of the enamines (**17**) (step ⑥ in Scheme 3) or by conrotatory ring opening of the aziridine ring in the aziridines (**22**). To our opinion the formation of the cyclobutane derivatives of the b-series is best described by an intramolecular [1,5] electrocyclization of the intermediate (**18**) (step ⑦ in Scheme 3), because we can explain the stereochemical outcome in the products by successfully applying the Woodward Hoffmann rules to this process.

In the examples, where X=NMe, the enamines (**17**) are 1,2-dihydroquinoline derivatives, which are known to be sensitive to oxidants, especially when the C-2-atom is unsubstituted or only bears one substituent.[4,22] Therefore the oxidation side reaction leading to quinolinium *p*-toluenesulfonates (**19-21**) in the presence of air is not surprising.

An alternative reaction pathway for the anils (**16**) is the 6π electrocyclic rearrangement (step ② in Scheme 3) followed by a rapid [1,5] H shift (step ③ in Scheme 3) leading to spirocyclic 1*H*- or 1'*H*-quinolines (**7a, 8a, 11a** and **12a**) (≅ '6π route').

Scheme 2



Scheme 3

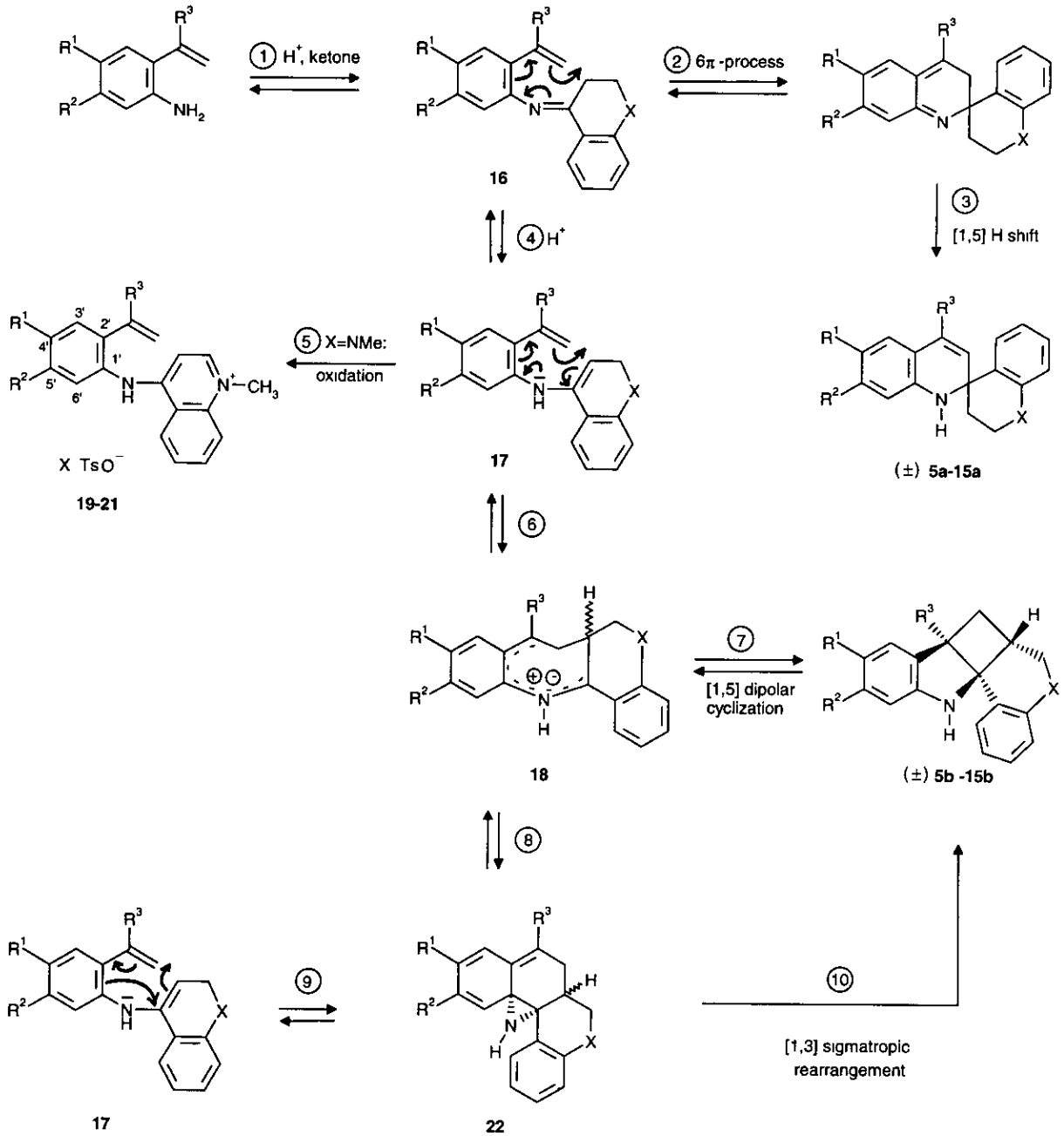

① H+, ketone
② 6π -process
③ [1,5] H shift
④ H+
⑤ X=NMe: oxidation
⑥
⑦ [1,5] dipolar cyclization
⑧
⑨
⑩ [1,3] sigmatropic rearrangement
16
17
18
22
19-21
X TsO−
(±) 5a-15a
(±) 5b -15b

Table 3 Expected Products in Acid Catalyzed Reactions of 2-Vinylanilin Derivatives with several Ketones

2-Vinylaniline Derivative			Ketone	Expected Product(s)	Lit.
R^1	R^2	R^3			
H	H	Me	acylated aromatic or heterocyclic compound	1*H*-quinoline- and/or cyclobut[*b*]indol	[1][22]
H	H	Me, Ph	cyclohexanone and substituted cyclohexanones	1*H*-quinoline	[17][24]
H, Cl	H	Me, Ph	*N*-substituted piperidin-4-one	cyclobut[1,2-*b*]indol	[9]
H	H	Me	α-tetralone	cyclobut[*b*]indole	this work
H	Cl	Me	α-tetralone	1*H*-quinoline and cyclobut[*b*]indole	this work
H, Cl	H	Ph	α-tetralone	1*H*-quinoline	this work
H	H, Cl	Me	4-chromanone	1'*H*-quinoline and cyclobut[*b*]indol	this work
H, Cl	H	Ph	4-chromanone	1'*H*-quinoline	this work
H	H, Cl	Me, Ph	1-methyl-2,3-dihydro-1*H*-quinoline-4-one	cyclobut[*b*]indole and 1-methylquinolinium *p*-toluenesulfonates	this work

Cationic intermediates such as iminium ions from an acid catalyzed process cannot be excluded with certainty. We are still at the beginning in understanding which factors influence the '6π route' and '[1,5] dipole route'. However, some rules of thumb can be infered from our experimental results and these are summarized in Table 3 and discussed in the conclusion.

CONCLUSION

One major observation made during these investigations is the strong '[1,5] dipole-route'-directing effect of the *N*-Me or *N*-Bzl group in para position to the carbonyl group bearing C-atom in cyclic ketones such as piperidin-4-ones and 2,3-dihydroquinolin-4-ones, which shows that the substitution pattern of the 2-vinylaniline derivatives has only subordinate relevance for the selectivity in these experiments. Another important result is the '6π route'-selectivity, when 2-(1-phenylvinyl)anilines (**3**) and (**4**) are used in the reactions with acetophenones and α-tetralone. The use of 2-isopropenylanilines (**1**) and (**2**) in the same reactions often provides reaction mixtures of spirocyclic 1*H*-quinolines and cyclobut[*b*]indoles.[1] This shows that the '6π route'-directing effect is determined by the ortho-vinylphenyl group. These results show, that if suitable ketones and 2-vinylanilines are chosen for the acid catalyzed procedure, several new complex heterocycles are formed, which would otherwise only be available from multistep synthesis, if at all. Further investigations in our laboratories are in progress with the aim to understand which features influence the selectivity in acid catalyzed reactions of 2-vinylaniline derivatives with ketones.

EXPERIMENTAL SECTION

General. For the synthesis of 2-(1-vinyl)anilines (**1-4**) see references 5,6 and 8. For the synthesis of 2,3-dihydro-1-methyl-1*H*-quinoline-4-one see reference 25.

Melting points were measured on a Büchi B-510 apparatus and are uncorrected. ^{1}H-Nmr spectra were taken on a 400 MHz-Bruker AM 400 spectrometer. ^{13}C-Nmr spectra were recorded on a 100.6 MHz-Bruker AM 400 instrument. Chemical shifts are reported in ppm referenced to TMS (^{1}H nmr) and $CDCl_3$ or DMSO-d_6 (^{13}C nmr). Infrared spectra (ir) were recorded by using a Bruker IFS 48 spectrophotometer. Mass spectra (ms) were obtained on a Finnigan MAT 212/SS 300 spectrometer. Thin layer chromatogtaphy (tlc) was performed on Merck silica gel 60F-254.

Standard Procedure for the Synthesis of Compounds (5-15). A mixture of 2-vinylaniline derivative (10 mmol), cyclic ketone (10-13 mmol), TsOH (Merck, 0.10 g) and absolute toluene (30 ml) was heated under reflux (Dean-Stark trap) for 12-18 h (see Table 1). The mixture was evaporated and the residue

purified either by flash-chromatographxy (FC; SiO_2, EtOAc/hexane 1:9 to 1:14 or Et_2O/hexane 1:9 or 1:10) or by recrystallization of either the free amine or the corresponding hydrochlorides, which were prepared by adding *ca.* 4.5N HCl/EtOH (10 ml) to the evaporated residues. In some cases, chromatography as well as recrystallization was used to obtain analytical pure samples.

Isolation and Purification of the Byproducts (19-21). When 2,3-dihydro-1-methyl-1*H*-quinolin-4-one was used in the procedure described above, the formation of quinolinium *p*-toluenesulfonates could be observed. Their isolation from the crude reaction mixture turned out to be simple, because these compounds are not soluable in toluene and a simple filtration afforded the crude products. To get almost analytical pure samples, recrystallizations from EtOAc, EtOAc/hexane 1:1 or Et_2O were necessary.

(±)-(6*aSR*, 7*aRS*, 12*aRS*)-5,6-Dihydro-7a-methyl-12*H*-naphthalene[1',2':1,4]cyclobut[1,2-*b*]indole (5b). Purified by FC (EtOAc/hexane 1:14): mp 149-151°C; ir (KBr, cm^{-1}) 3379, 3015, 2955, 1603, 1483, 1456, 1385, 1321, 1074, 744; ^1H nmr ($CDCl_3$) δ 0.88 (s, 3H, C-7a-Me), 1.63-1.73 (m, H-5 and H-6), 1.91 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.26 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.79 (dt, J=16.0, ,4.0 Hz, 1H, H-5 or H-6), 2.86-3.00 (m, 2H, H-6a, H-5 or H-6), 4.18 (s, NH), 6.69 (dm, J=7.0 Hz, 1H, H-11), 6.78 (td, J=7.0, 1.0 Hz, 1H, H-9), 7.05 (dm, J=7.0 Hz, 1H, H-8), 7.10 (td, J=7.0, 1.0 Hz, 1H, H-10), 7.18-7.27 (m, 3H, H-2 - H-4), 7.58 (m, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.64, 22.71, 26.39, 35.91 (C-7), 39.87 (C-6a), 52.57 (C-7a), 67.42 (C-12a), 109.30, 118.75, 123.52, 126.03, 126.56, 127.70, 128.30, 128.40, 136.39, 137.42, 138.38, 150.43 (C-11a); HRms, *m/z* Calcd for $C_{19}H_{19}N$: 261.1517. Found 261.1518; Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.18; H, 7.41; N, 5.29.

(±)-(6*aSR*, 7*aRS*, 12*aRS*)-7-Chloro-5,6-dihydro-7a-methyl-12*H*-naphthalene[1',2':1,4]cyclobut[1,2-*b*]-indole (6b). Purified by FC (EtOAc/hexane 1:10) and recrystallization of the hydrochloride from AcOEt/-EtOH 5:1: mp 96-97°C; (free amine); ir (KBr, cm^{-1}) 3360, 2972, 2934, 2849, 1599, 1483, 1437, 1321, 1065, 906, 833, 798, 766; ^1H nmr ($CDCl_3$) δ 0.85 (s, 3H, (-7a-Me), 1.66-1.73 (m, 2H, H-5 and H-6), 1.91 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.24 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.79 (dt, J= 16.0, 4.0 Hz, 1H, H-5 or H-6), 2.86-3.0 (m, 2H, H-6a, H-5 or H-6), 4.25 (s, 1H, NH), 6.63 (d, J=2.0Hz, 1H, H-11), 6.71 (dd. J=8.0, 2.0 Hz. 1H, H-9). 6.92 (d, J=8.0 Hz, 1H, H-8), 7.19-7.25 (m, 3H, H-2-H-4), 7.52 (m, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.61, 22.76, 26.37, 35.99 (C-7), 40.14 (C-6a), 51.98 (C-7a), 68.09 (C-12a), 109.14, 118.40,

124.29, 126.28, 126.83, 128.16, 128.53, 133.19, 135.89, 136.0, 138.46, 151.65 (C-11a), Elms, $^{m}/_{z}$ (rel. inten.) 295 (M^+ (^{35}Cl), 100), 280(84), 266(40), 252(24), 219(24); HRms, $^{m}/_{z}$ Calcd for $C_{19}H_{18}NCl$: 295.1127. Found 295.1119; Anal. Calcd for $C_{19}H_{18}NCl$: C, 77.15; H, 6.13; N, 4.74; Cl, 11.98. Found: C, 77.28; H, 6.21; N, 4.62; Cl, 11.86.

(±)-3',4'-Dihydro-4-phenylspiro[(2'*H*)-naphthalene-1',2(1*H*)quinoline] (7a). Purified by FC (EtOAc/-hexane 1:12): mp 61-63°C; ir (KBr, cm^{-1}) 3383, 3018, 1634, 1601, 1487, 1466, 1313, 1263, 752, 702; ^1H nmr ($CDCl_3$) δ 1.90 (m, 2H), 2.05 (m, 1H), 2.21 (m, 1H), 2.82 (m, 2H), 4.24 (s, 1H, NH), 5.59 (s, 1H, olefinic H), 6.47 (dd, J=8.0, 1.0 Hz, 1H), 6.58 (td, J=8.0, 1.0 Hz, 1H), 6.96 (dd, J=8.0, 1.0 Hz, 1H), 7.02 (td, J=8.0, 1.0 Hz, 1H), 7.10 (dm, J=8.0 Hz, 1H), 7.15-7.25 (m, 2H), 7.30-7.45 (m, 5H), 7.82 (dm, J=8.0 Hz 1H); ^{13}C nmr ($CDCl_3$) δ 17.90, 29.51, 38.11, 56.07 (spiro-Cq), 112.99, 116.84, 119.77, 125.92, 126.30, 127.09, 128,59, 128.86, 128.93, 129.25 (olefinic C-3), 130.23, 135.45, 135.51, 139.47, 142.53, 142.96; EIms, $^{m}/_{z}$ (rel. inten.) 323 (M^+, 44), 294(100), 218(82), 148(20); HRms, $^{m}/_{z}$ Calcd for $C_{24}H_{21}N$ 323.1673. Found 323.1670; Anal. Calcd for $C_{24}H_{21}N$: C, 89.13, H, 6.54; N, 4.33. Found: C, 89.0; H, 6.64; N, 4.23.

(±)-6-Chloro-3',4'-dihydro-4-phenylspiro[(2'*H*)-naphthalene-1',2(1*H*)quinoline] (8a). Purified by FC (EtOAc/hexane 1:14) and recrystallization of the free amine from hexane: mp 159-160°C; ir (KBr, cm^{-1}) 3391, 2934, 1597, 1485, 1443, 1310, 1271, 885, 810, 795, 702; ^1H nmr ($CDCl_3$) δ 1.90 (m, 2H,) 2.03 (m, 1H), 2.20 (m, 1H), 2.83 (m, 1H), 4.26 (s, 1H, NH), 5.62 (d, J=1.0 Hz, 1H, olefinic H-3), 6.39 (d, J=8.0 Hz, 1H, 6.92 (d, J=2.0 Hz, 1H), 6.97 (dd, J=8.0, 2.0 Hz, 1H), 7.11 (dm, J=8.0 Hz, 1H), 7.15-7.25 (m, 2H), 7.13-7.43 (m, 5H), 7.78 (dm, J=8.0 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 17.93, 29.49, 38.22, 56.27 (spiro-Cq), 114.05, 121.27, 121.48, 125.53, 126.43, 127.33, 127.59, 128.37, 128.50, 128.77, 128.85, 130.12, 130.33, 134.81, 135.52 (olefinic C-4), 138.78, 141.10, 142.55; EIms $^{m}/_{z}$ (rel. inten.) 357 (M^+ (^{35}Cl), 58), 330(48), 329(66), 328(100), 252(60), 146(16); Anal. Calcd for $C_{24}H_{20}NCl$: C, 80.55; H, 5.63; N, 3.91; Cl, 9.91. Found: C, 80.48; H, 5.67; N, 3.94; Cl, 9.87.

(±)-(6*a*-*RS*, 7*aRS*, 12*aRS*)-6,12-Dihydro-7a-methylindolo[2',3':2,3]cyclobut[1,2-*c*]chroman (9b). Purified by FC (EtOAc/hexane 1:10) and recrystallization of the free amine from hexane: mp 133-135°C; ir (KBr, cm^{-1}) 3373, 3042, 2964, 2847, 1609, 1483, 1460, 1261, 1217, 1090, 773, 746; ^1H nmr ($CDCl_3$) δ 0.83 (s, 3H, C-7a-Me), 2.11 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.32 (dd, J=11.3, 9.4 Hz, 1H, H-7), 2.92 (tdd, J=9.4, 3.0, 1.5 Hz, 1H, H-6a), 3.82 (dd, J=11.3. 3.0 Hz, 1H, H-6), 4.01 (dd, J=11.3, 1.5 Hz, 1H, H-6),

4.19 (s, 1H, NH), 6.74 (dm, J=8.0 Hz, H-11), 6.82 (td, J=7.0, 1.0 Hz, 1H, H-8), 7.01 (m, 2H, H-2 and H-4), 7.10 (m, 1H, H-8), 7.14 (m, 1H, H-10), 7.23 (m, 1H, H-3), 7.57 (dd, J=8.0, 2.0 Hz, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.74, 34.0 (C-7), 41.97 (C-6a), 52.03 (m, C-7a), 64.66 (C-12a), 65.37, 110.09, 117.35, 119.40, 121.32) 123.78, 124.04, 127.97, 128,24, 128.69, 137.03, 149.65, 155.94; EIms, $^{m}/_{z}$ (rel. inten.) 263 (M^+, 80), 222(100), 85(42). 83(64); HRms, $^{m}/_{z}$ Calcd for $C_{18}H_{17}NO$: 263.1310. Found: 263.1314; *Anal. Calcd for* $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.01; H, 6.60; N, 5.42.

(±)-(6*aRS*, 7*aRS*, 12*aRS*)-7-Chloro-6,12-dihydro-7a-methylindolo[2',3':2,3]cyclobut[1,2-*c*]chroman (10b). Purified by FC (EtOAc/hexane 1:10) and recrystallization of the free amine from Et_2O/hexane 1:5: mp 150-152°C; ir (KBr, cm^{-1}) 3375, 2959, 2922, 1605, 1591, 1481, 1437, 1335, 1219, 1138, 1124, 997, 912, 839, 766; ^{1}H nmr ($CDCl_3$) δ 0.80 (s, 3H), 2.10 (dd, J=11.0, 9.0 Hz, 1H, H-7), 2.29 (dd, J=11.0, 9.0 Hz, 1H, H-7), 2.91 (tdd, J=9.0, 2.0, 1.0 Hz, 1H, H-6a), 3.81 (dd, J=12.0, 1.0 Hz, 1H, H-6), 4.01 (dd, J=12.0, 1.0 Hz, 1H, H-6), 4.26 (s, 1H, NH), 6.68 (d, J=2.0 Hz, 1H, H-11), 6.75 (dd, J=8.0, 2.0 Hz, 1H, H-9), 6.97 (d, J=8.0 Hz, 1H, H-8), 6.99-7.04 (m, 2H, H-2 and H-4), 7.24 (td, J=8.0, 2.0 Hz, H-3), 7.52 (dd, J=8.0, 2.0 Hz, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.65, 34.05 (C-7), 42.22 (C-6a), 51.51 (m, C-7a), 65.29 (C-12a), 65.40, 110.0, 117.50, 119.15, 121.48, 124,82, 128.51, 128.56, 133.49, 135.59, 150.90 (C-11a), 155.98; HRms, $^{m}/_{z}$ Calcd for $C_{18}H_{16}NOCl$: 297.0920. Found 297.0915; *Anal. Calcd for* $C_{18}H_{16}NOCl$: C, 72.6; H, 5.42; N, 4.70; Cl, 11.91. Found: C, 71.69; H, 5.49; N, 4.68; Cl, 11.81.

(±)-2,3-Dihydro-4'-phenylspiro[chroman-4,2'(1'H)*quinoline*] (11a). *Purified* by FC (EtOAc/hexane 1:12) and recrystallization of the free amine from hexane in the cold: mp 164-166°C; ir (KBr, cm^{-1}) 3379, 3028, 1601, 1487, 1448, 1323, 1217, 1217, 1051, 756, 706; ^{1}H nmr ($CDCl_3$) δ 2.23 (m, 1H), 2.32 (m, 1H), 4.20-4.40 (m, 3H), 5.59 (d, J=2.0 Hz, 1H, olefinic H-3'), 6.53 (dd, J=8.0, 2.0 Hz, 1H), 6.61 (td, J=8.0, 2.0 Hz, 1H), 6.83 (dd, J=8.0, 2.0 Hz, 1H), 6.97 (dd, J=8.0, 2.0 Hz, 1H), 7.05 (td, J=8.0, 2.0 Hz, 1H), 7.18 (ddd, J=8.0, 7.0, 2.0 Hz. 1H), 7.30-7.45 (m, 5H), 7.70 (dd, J=8.0, 2.0 Hz, 1H); ^{13}C nmr ($CDCl_3$) δ 37.39, 52.48 (spiro-Cq), 61.64, 113.44, 116.86, 117.50, 119.92, 120.96, 126.21, 127.51, 127.55, 128.23 (2C), 128.96 (2C), 129.03, 129.10, 129.13, 130.20, 136.85, 139.14, 142.04, 153.09; EIms, $^{m}/_{z}$ (rel. inten.) 325 (M^+, 12), 297(100); Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.61; H, 5.91; N, 4.21.

(±)-6'-Chloro-4'-phenylspiro[chroman-4,2'(1'*H*)quinoline] (12a). Purified by FC (EtOAc/hexane 1:10) and recrystallization of the free amine from hexane/Et_2O 10:1: mp 172-173°C; ir (KBr, cm^{-1}) 3379, 1585, 1481, 1448, 1312, 1258, 1049, 814, 775, 704; ^1H nmr ($CDCl_3$) δ 2.20 (s, 1H), 2.30 (m,1H), 4.22 (m, 1H), 4.27 (s, 1H, NH), 4.32 (m, 1H), 5.62 (s, 1H), 6.45 (d, J=8.0 Hz, 1H), 6.83 (dd, J=8.0, 2.0 Hz,, 1H), 6.92 (ddd, J=8.0, 7.0, 2.0 Hz, 1H), 6.93 (d, J=2.0 Hz), 6.98 (dd, J=8.0, 2.0 Hz, 1H), 7.18 (ddd, J=8.0, 7.0, 2.0 Hz, 1H), 7.35-7.45 (m, 5H), 7.64 (dd, J=8.0, 1.0 Hz, 1H). ^{13}C nmr ($CDCl_3$) δ 37.41, 52.61 (spiro-Cq), 61.54, 114.49, 116.98, 121.04, 121.32, 122.15, 125.76, 127.81, 128.45, 128.56, 128.59, 128.74, 128.82, 129.28, 130.04, 136.08, 138.41, 140.57, 153.03; HRms, $^m/_z$ Calcd for $C_{23}H_{18}NOCl$: 359.1076. Found 359.1071. Anal. Calcd for $C_{23}H_{18}NOCl$: C, 76.77; H, 5.04; N, 3.89; Cl, 9.85. Found: C, 76.63; H, 5.14; N, 3.86; Cl, 9.75.

(±)-(6*aRS*, 7*aRS*, 12*aRS*)-6,12-Dihydro-5,7a-dimethylindolo[2',3':2,3]cyclobut[1,2-*c*]quinoline (13b). Purified by FC (EtOAc/hexane 1:10): mp 123-124°C; ir (KBr, cm^{-1}) 3344, 2957, 2916, 1603, 1495, 1490, 1481, 1325, 1285, 1205, 1040, 750; ^1H nmr ($CDCl_3$) δ 0.84 (s, 3H, C-7a-Me), 2.10 (dd, J=11.0, 9.0 Hz, 1H, H-7), 2.27 (dd, J=11.0, 9.0 Hz, 1H, H-7), 2.82 (dd, J=10.0, 4.0 Hz, 1H, H-6), 2.92 (dd, J=10.0, 4.0 Hz, 1H, H-6), 2.94 (s, 3H, NMe), 2.94 (m, 1H, H-6a), 4.16 (s, 1H, NH), 6.70 (dm, J=7.0 Hz, 1H, H-11), 6.78 (td, J=7.0, 1.0Hz. 1H, H-9), 6.78-6.84 (m, 2H, H-2 and H-4), 7.06 (dm, J=7.0Hz, 1H, H-8), 7.10 (td, J=7.0, 1.0 Hz, H-10), 7.23 (td. J=7.0, 2.0 Hz, 1H, H-3), 7.53 (dd, J=7.0, 2.0 Hz, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.65, 35.71 (C-7). 39.88 (NMe), 42.76 (C-6a), 51.29, 52.02 (C-7a or C-12a), 65.92 (C-7a or C-12a), 109.61, 111.85, 117.59, 118.91, 123.75, 123.81, 127.76, 127.84, 128.48, 137.53, 148.18, 149.90; EIms, $^m/_z$(rel. inten.) 276 (M^+, 49), 275 (M^+-H, 100), 261(15); HRms, $^m/_z$ Calcd for $C_{19}H_{20}N_2$: 276.1626. Found 276.1622; Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.50; H, 7.30; N, 10.05.

(±)-(6*aRS*, 7*aRS*, 12*aRS*)-7-Chloro-6,12-dihydro-5,7a-dimethylindolo[2',3:2,3]cyclobut[1,2-*c*]quinoline (14b). Purified by FC (Et_2O/hexane 1:10) and recrystallization of the free amine from hexane: mp 140-142°C; ir (KBr, cm^{-1}) 3375, 2930, 2808, 1599, 1479, 1447, 1323, 1283, 1207, 1067, 1040, 910, 841, 795, 760; ^1H nmr ($CDCl_3$) δ 0.80 (s, 3H, C-7a-Me), 2.08 (dd, J=11.0, 9.0 Hz, 1H, H-7), 2.23 (dd, J=11.0,

9.0 Hz, 1H, H-7), 2.82 (dm, J=14 Hz, 1H, H-6), 2.93 (dm, J=14 Hz, 1H, H-6), 2.93 (s, 3H, NMe), 2.94 (m, 1H, H-6a), 4.23 (s, 1H, NH), 6.64 (d, J=2.0 Hz, 1H, H-11), 6.71 (dd, J=8.0, 2.0 Hz, 1H, H-9), 6.80 (dm, J=7.0 Hz, 1H, H-4), 6.81 (td, J=7.0, 1.0 Hz, 1H, H-2), 6.92 (d, J=8.0 Hz, 1H, H-8), 7.23 (td, J=7.0, 2.0 Hz, 1H, H-3), 7.48 (dd, J=7.0, 2.0 Hz, 1H, H-1); ^{13}C nmr ($CDCl_3$) δ 22.52, 35.75 (C-7), 39.89 (NMe), 42.99 (C-10a), 51.29, 51.40 (C-7a or C-12a), 66.53 (C-7a or C-12a), 109.43, 111.99, 117.72, 118.55, 123.32, 124.50, 128.09, 128.36, 133.19, 136.06, 148.20, 151.12; EIms, $^{m}/_{z}$ (rel. inten.) 309 (M^+(^{35}Cl), 100) 295(14), 144(12); Anal. Calcd for $C_{19}H_{19}N_2Cl$: C, 73.40; H, 6.16; N, 9.01; Cl, 11.40. Found: C, 73.31; H, 6.26; N, 9.03; Cl, 11.45.

(±)-(6*aRS*, 7*aSR*, 12*aRS*)-6,12-dihydro-5-methyl-7a-phenylindolo[2',3':2,3]cyclobut[1,2-*c*]quinoline (15b). Purified by FC (EtOAc/hexane 1:9) and recrystallization of the free amine by EtOAc/hexane 1:8: mp 177-179°C; ir (KBr, cm^{-1}) 3356, 3026, 2926, 2806, 1601, 1495, 1462, 1373, 1283, 1205, 1040, 750, 698; ^{1}H nmr ($CDCl_3$) δ 2.37 (dd, J=10.0, 8.0 Hz, 1H, H-7), 2.96 (s, 3H, NMe), 2.97 (m, 2H, H-6 and H-7), 3.05 (dd, J=19.0, 9.0 Hz, 1H, H-6), 3.09 (tt, J=9.0, 2.0 Hz, 1H, H-6a), 4.21 (s, 1H, NH), 6.44 (td, J=8.0, 1.0 Hz, 1H, arom. H), 6.66 (dd, J=8.0, 1.0 Hz, 1H, arom. H), 6.78-6.87 (m, 4H, arom. H's), 6.93-7.06 (m, 5H, arom.- H's). 7.10 (dd, J=8.0, 2.0Hz, 1H, arom. H), 7.19 (td, J=8.0, 2.0Hz, 1H, arom. H); ^{13}C nmr ($CDCl_3$) δ 31.14 (C-7), 39.95 (NMe), 41.70 (dm, C-6a), 51.10, 60.87 (C-7a or C-12a), 69.59 (C-7a or C-12a), 110.44, 111.51, 117.27, 119.61, 122.38, 125.65, 126.13, 127.27, 127.73, 128.14, 129.0, 137.22, 141.98, 148.09, 150.63; EIms, $^{m}/_{z}$ (rel. inten.) 338 (M^+, 74), 337(100), 168(14), 144(14); Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.50; H, 6.60; N, 8.18.

4-(2-Isopropenylphenyl)amino-1-methylquinolinium *p*-toluenesulfonate (19). Purified by recrystallization from EtOAc/hexane 1:1: mp 175-176°C; ir (KBr, cm^{-1}) 3100, 3055, 1620, 1556, 1491, 1404, 1227, 1167, 1119, 1032, 1011, 828, 764, 679; ^{1}H nmr (DMSO-d_6) δ 1.96 (s, 3H), 2.27 (s, 3H), 4.15 (s, 3H, N^+-Me), 5.02 (m, 1H, olefinic H), 5.06 (m, 1H, olefinic H), 6.28 (d, J=8.0 Hz, 1H), 7.09 (d, J=8.0 Hz, 2H), 7.41 (m, 1H, arom. H), 7.46 (m, 2H), 7.53 (m, 3H, arom. H's), 7.88 (m, 1H), 8.13 (m, 1H), 8.51 (d, J=8.0Hz, 1H), 8.73 (d, J=8.0Hz, 1H), 10.81 (s, 1H, NH); ^{13}C nmr (DMSO-d_6) δ 20.71 (Me), 22.91 (Me), 42.22 (NMe), 99.97, 116.62, 117.40, 118.0, 123.86, 125.43, 127.25, 127.99, 128.33, 128.86, 129.07, 129.67, 133.42, 137.61,138.62, 141.03, 141.78, 145.59, 147.57, 155.25; FAB-HRms (positive mode), $^{m}/_{z}$

Calcd for $C_{19}H_{19}N_2$: 275.1541. Found 275.1548; Anal. Calcd for $C_{26}H_{26}N_2O_3S$: C, 69.93; H, 5.87; N, 6.27. Found: C, 69.92; H, 5.92; N, 6.16.

1-Methyl-4-[2-(1-phenylvinyl)phenyl]aminoquinolinium *p*-toluenesulfonate (20). Purified by recrystallization form Et_2O: mp 176-179°C; ir (KBr, cm^{-1}) 3452, 3053, 1620, 1553, 1485, 1404, 1177, 1121, 1034, 1011, 766, 681; ^1H nmr (DMSO-d_6) δ 2.27 (s, 3H), 4.09 (s, 3H, NMe), 5.42 (s, 1H, olefinic H), 5.55 (s, 1H, olefinic H), 6.29 (d, J=7.0 Hz, 1H), 6.93-7.08: (m, 5H, arom. H's), 7.09 (d, J=8.0 Hz, 1H, arom. H), 7.17 (t, J=8.0 Hz, 1H, arom. H), 7.41 (d, J=8.0 Hz, 1H, arom. H), 7.46 (d, J=8.0 Hz, 1H, arom. H), 7.55-7.68 (m, 4H, arom. H's), 7.55-7.68 (m, 4H, arom. H's), 8.01 (m, 2H, arom. H's), 8.12 (d, J=8.0Hz, 1H, arom. H); ^{13}C nmr (DMSO-d_6) δ 20.73 (Me), 42.03 (NMe), 100.45, 117.55, 117.84 (olefinic C), 118.22, 123.71, 125.46 (2C), 126.23 (2C), 126.53, 127.36, 127.96, 128.0 (2C), 128.11, 129.69, 131.59, 133.96, 137.59, 138.32, 138.94, 139.98, 145.67, 146.59, 146.88, 154.36; FAB-HRms (positive mode), $^m/_z$ Calcd for $C_{24}H_{21}N_2$: 337.1704. Found 337.1705; Anal. Calcd for $C_{31}H_{28}N_2O_3S$: C, 72.3; H, 5.55; N, 5.51. Found: C, 72.16; H, 5.49; N, 5.57.

[4-Chloro-[2-(1-phenylvinyl)phenyl]amino-1-methylquinolinium *p*-toluenesulfonate (21). Purified by recrystallization from EtOAc: mp 178-183°C; ir (KBr, cm^{-1}) 2924, 1661, 1618, 1502, 1429, 1344, 1105, 1069, 816, 756; ^1H nmr (DMSO-d_6) δ 2.32 (s, 3H), 3.93 (s, 3H, NMe), 5.37 (s, 1H, olefinic H), 5.39 (s, 1H, olefinic H), 6.08 (d, J=8.0Hz, 1H), 6.79 (d, J=8.0Hz, 2H), 6.86 (t, J=8.0Hz, 2H), 6.95 (tt, J=8.0, 9.0Hz, 1H), 7.09 (d, J=8.0Hz, 2H), 7.28 (m, 2H), 7.34 (t, J=8.0Hz, 1H), 7.45 (d, J=8.0Hz, 1H), 7.47 (d, J=2.0Hz, 1H), 7.66 (d, J=8.0Hz, 2H), 7.70 (m, 1H), 8.11 (d, J=8.0Hz, 1H), 8.31 (d, J=8.0Hz, 1H), 10.52 (s, 1H, NH); ^{13}C nmr (DMSO-d_6) δ 21.17 (Me), 42.14 (NMe), 100.73, 116.42, 117.87, 118.84 (olefinic C), 125.55, 125.81 (2C), 126.34 (2C), 126.73, 127.56, 128.11, 128.33, 129.25, 129.80 (2C), 131.26, 132.98, 133.91, 133.96, 138.07, 139.19, 139.33, 140.48, 145.93, 146.58, 154.85 (olefinic C); FAB-HRms (positive mode), $^m/_z$ Calcd for $C_{24}H_{20}N_2Cl$: 371.1308. Found 371.1315; Anal. Calcd for $C_{31}H_{27}N_2O_3ClS$: C, 68.56; H, 5.01; N, 5.16. Found: C, 68.43; H, 4.97; N, 5.09.

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