Azirine/Oxindole Ring Enlargement *via* Amidinium Intermediates

by **Maged K. G. Mekhael**[a])[b])[1]), **Stefan Bienz**[a]), **Anthony Linden**[a]), and **Heinz Heimgartner***[a])

[a]) Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
[b]) Mubarak City for Scientific Research and Technological Applications, Alexandria, Egypt

A novel general method for the synthesis of oxindoles, namely the 'azirine/oxindole ring enlargement *via* amidinium-intermediates' has been established: the reaction of 2*H*-azirin-3-amines **1** with $BF_3 \cdot OEt_2$ in THF solution at $-78°$ leads to 1,3,3-trialkyl-2-amino-3*H*-indolium tetrafluoroborates **14** in good yields (*Scheme 5*). Treatment of aqueous solutions of **14** at 0° with aqueous NaOH (30%) and extraction with CH_2Cl_2 gives oily substances that are either hydrates of 1,3,3-trialkyl-2-dihydroindol-2-imines **15** or the corresponding indolium hydroxides. These products are transformed to the corresponding 1,3,3-trialkyl-2,3-dihydroindol-2-ones **17** in modest yields upon refluxing in H_2O/THF. Reaction of **14** with Ac_2O in pyridine at *ca.* 23° for 16 h followed by aqueous workup and chromatographic separation leads to mixtures of *N*-(1,3,3-trialkyl-2,3-dihydro-indol-2-yliden)acetamides **16** and oxindoles **17** (*Scheme 6*). Hydrolysis of **16** with aqueous HCl under reflux for 1–2 h gives oxindoles **17** in a good yield. Several oxindoles, spiro-oxindoles, and 5-substituted oxindoles were synthesized by means of the reactions mentioned above.

Introduction. – Among numerous methods for the synthesis of oxindoles, considerable attention has been given to reactions in which appropriate precursors with a side chain containing a reactive center suitably positioned for the construction of the heterocyclic ring are subjected to cyclization at the *ortho*-position of the aromatic ring [1–7]. Recently, we showed that the *N*-phenyl residue of 2*H*-azirin-3-amines of type **1** (R^4 = Ph) with its free *ortho*-position is able to act as an internal nucleophile under the influence of the *Lewis* acid BF_3, thereby leading to the corresponding indolium tetrafluoroborate. The latter was converted subsequently to oxindole derivatives [8]. Of special interest are those oxindole derivatives bearing an allyl substituent at C(3), as they are regarded as versatile starting materials for the preparation of 3-(aminoethyl)-1,3-dimethyloxindole, which can be converted to desoxynoreseroline, the basic ring structure of the alkaloid physostigmine, which has a well-established pharmacological activity [9] (and lit. cit. therein).

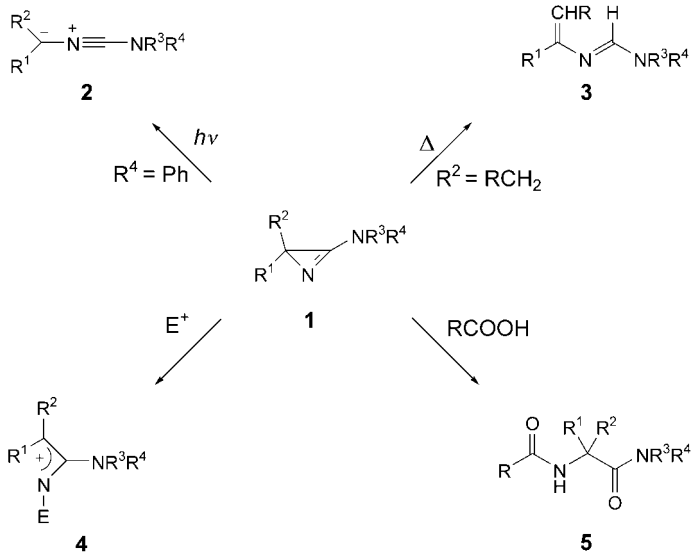
The first synthesis of 2*H*-azirin-3-amines **1** has been described by *Rens* and *Ghosez* [10]. These strained cyclic amidines proved to be versatile building blocks for the preparation of heterocycles, as well as peptides containing α,α-disubstituted glycines [11]. It has been shown that each of the three ring bonds can be cleaved selectively depending on the reaction conditions, leading to reactive intermediates such as nitrile ylides **2** and N^2-ethenylformamidines **3** (C,C cleavage), and 1,1-diaminoethenyl ('1-azaallyl') cations **4** (C,N cleavage; *Scheme 1*). In the case of the cleavage of the C=N bond, α-amino acid derivatives **5** are formed *via* an intermediate aziridine (*cf.* [11]). For example, reactions of azirines **1** with carboxylic acids [10][12–14] proceed by

[1]) Part of the Ph.D. thesis of *M. K. G. M.*, Universität Zürich, 2003.

© 2004 Verlag Helvetica Chimica Acta AG, Zürich

protonation and addition of the carboxylate onto the amidinium intermediate formed, yielding an aziridine, which rearranges *via* ring opening to give an *N*-acylamino carboxamide (*cf.* [14–17] and refs. cit. therein). On the other hand, reactions of **1** with NH-acidic heterocycles ($pK_a < 8$) lead to new heterocycles with a ring enlarged by three atoms (N–C–C) [18][19], *e.g.*, 3-oxo sultams of different ring size [20–24].

Scheme 1



The reaction of **1** with trifluoroacetamide gives 4*H*-imidazoles [25]. A serious limitation of this reaction is the low acidity of carboxamides, as only substances with $pK_a < 8$ are able to activate **1** by protonation (pK_b of **1**, R^1–R^4 = Me: 7.1 [26]). Therefore, neither benzamide nor acetamide undergo a reaction with **1**. Recently, we were able to overcome this hurdle by activating **1** with the *Lewis* acid BF_3 [25]. The activation of **1** by treatment with BF_3 has also been used in reactions of **1** with enolates of esters, thioesters, and carboxamides to give 1,5-dihydro-2*H*-pyrrol-2-ones, and even the enolate of acetophenone reacts with the BF_3 complex of **1** leading to a 2*H*-pyrrol-3-amine derivative [27]. Furthermore, these complexes undergo reactions with α-amino acid esters in which 3,6-dihydropyrazin-2(1*H*)-ones are formed as the main product; the same products are obtained when 2*H*-azirin-3-amines **1** are reacted with α-amino acid ester hydrochlorides [28].

In the present paper, we describe the reactions of 2*H*-azirin-3-amines **1** (R^4 = Ph) containing an *N*-Ph residue with BF_3 in the absence of external nucleophiles to give 2,3-dihydro-1*H*-indol-2-ones (indoline-2-ones, oxindoles). The synthesis of spirocyclic oxindoles is considered as a generalization of this novel ring-enlargement reaction. Furthermore, new 2*H*-azirin-3-amines with a substituted *N*-Ph ring were synthesized and transformed to 5-substituted oxindoles, which are of special interest in alkaloid synthesis.

Results and Discussion. – 1. *Synthesis of 2*H-*Azirin-3-amines.* The carboxamides **6**, which are used as precursors in the azirine synthesis, were prepared by one of the following methods, depending on the availability of the starting materials (*Scheme 2*). In *Method A*, we started from commercially available acid chlorides **7**, which were reacted with the corresponding *N*-methylanilines. In the case of the carbocyclic derivatives **6c**–**6f**, the acid chlorides were prepared by treatment of the corresponding cycloalkane carboxylic acids **8** ($R^1-R^2=-(CH_2)_n-$) with $SOCl_2$ to give **7**. In *Method B*, carboxamides **9** were alkylated by subsequent treatment with LDA and an alkyl halide [29]. The prepared amides **6** are collected in *Table 1*.

Scheme 2

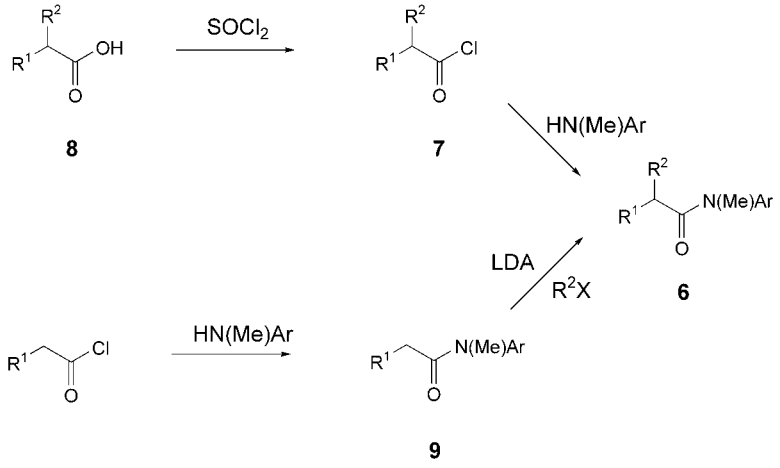


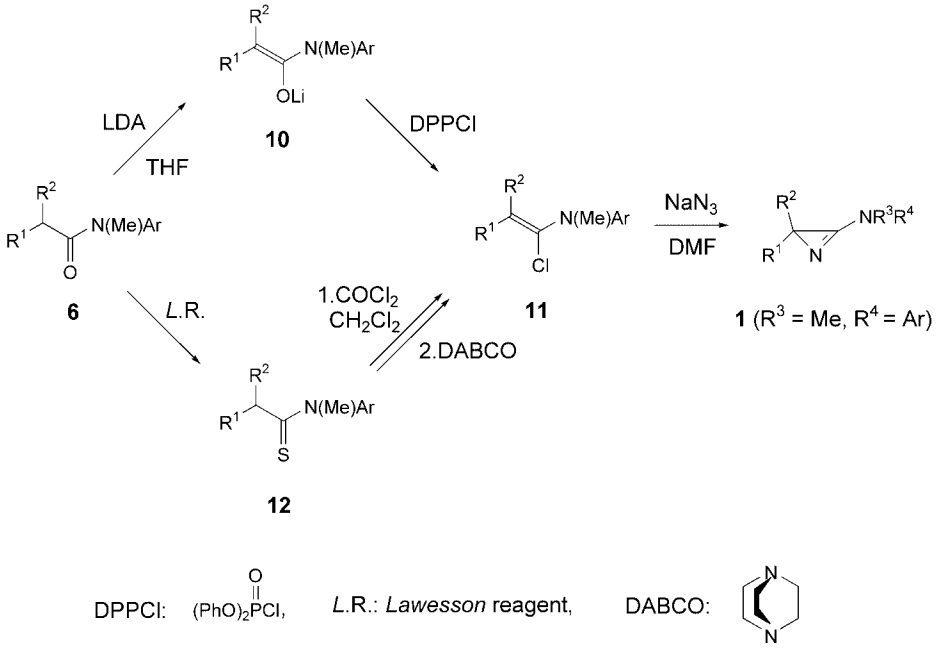
Table 1. *Synthesized Amides* **6** *and 2*H-*Azirin-3-amines* **1** (yields in [%])

	R^1	R^2	R^3	R^4	**6**	**1**
a	Me	$PhCH_2$	Me	Ph	78	83
b	Me	Me_2CHCH_2	Me	Ph	80	71
c	$-(CH_2)_3-$		Me	Ph	88	86
d	$-(CH_2)_4-$		Me	Ph	95	80
e	$-(CH_2)_5-$		Me	Ph	87	55
f	$-(CH_2)_6-$		Me	Ph	89	79
g	Me	Me	Me	4-MeO–C_6H_4	96	87
h	Me	Me	Me	4-NO_2–C_6H_4	87	56

The 2*H*-azirin-3-amines **1a**–**1h** were synthesized according to the following two methods. According to [30], a solution of an amide **6** in dry THF at 0° under an Ar atmosphere was treated with LDA, and, after 1 h, the amide enolate **10** formed was treated with diphenyl phosphorochloridate (diphenylphosphoryl chloride, DPPCl) at 0°. A smooth reaction took place, leading to the corresponding chloroenamines **11**. Under an Ar atmosphere, the suspension was filtered into a suspension of NaN_3 in dry

DMF. After 3–4 d at room temperature, the 2,2-disubstituted 2*H*-azirin-3-amines **1a**–**1g** were obtained (*Scheme 3* and *Table 1*).

Scheme 3



Compounds **1a**–**1f** have already been synthesized and fully characterized either by this method [30] or with $COCl_2$ according to the procedure described in [31]. The new azirine **1g** was fully characterized by spectroscopic methods and elemental analysis (see *Exper. Part*).

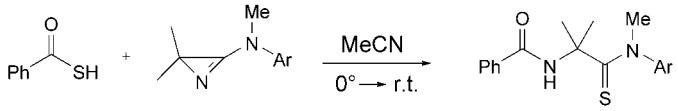
On the other hand, amide **6h** was treated with *Lawesson* reagent to give the corresponding thioamide **12h** in 87% yield (*cf.* [31]). The latter was subsequently dissolved in CH_2Cl_2 containing one drop of DMF, and a solution of $COCl_2$ in toluene was added dropwise at 0°. Then, the solvent was evaporated and the residue was dissolved in THF. After addition of 1,4-diaminobicyclo[2.2.2]octane (DABCO), the precipitate was separated by filtration, the solution containing the chloroenamine **11h** was evaporated, and a solution of NaN_3 in DMF was added. After 2 weeks, **1h** was obtained in 56% yield (*Scheme 3*).

It is worth mentioning that an improvement of the published method for synthesizing **1** *via* the thioamides [31–33] was achieved by performing the reaction of **11** with NaN_3 in DMF instead of THF and by increasing the reaction time to two weeks. Furthermore, the chloro-enamine **11h** could be isolated by carrying out the reaction of **12** (Ar = 4-NO_2–C_6H_4) with $COCl_2$ and DABCO in THF for 4 d.

The structures of the thioamide **12h**, the chloro-enamine **11h**, and the azirine **1h** were established on the basis of their spectroscopic data and elemental analyses. The IR spectra of the new azirines **1g** and **1h** showed a strong absorption band at 1753 and

1742 cm^{-1}, respectively, which is characteristic of the C=N stretching of the azirine ring. Furthermore, **1g** and **1h** were characterized chemically by making use of the characteristic reaction with thiobenzoic acid (*cf.* [33–38]). The resulting thioamides **13a** and **13b** were isolated, after chromatographic workup (SiO_2), in analytically pure form in 88 and 92% yield, respectively (*Scheme 4*).

Scheme 4



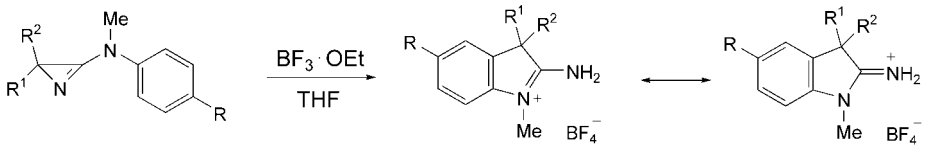
1g Ar = 4-MeO-C_6H_4 **13a** Ar = 4-MeO-C_6H_4

h Ar = 4-NO_2-C_6H_4 **b** Ar = 4-NO_2-C_6H_4

The structures of **13a** and **13b** were elucidated on the basis of their spectroscopic data. The IR spectra are characterized by strong absorption bands at 3258 and 3293 cm^{-1} for N–H, and at 1637 and 1642 cm^{-1}, respectively, for the amide C=O group. The ^{13}C-NMR spectra show *singlets* at 209.1 and 209.4 ppm for C=S, and 165.0 and 165.4 ppm for C=O, respectively. The Me groups of **13a** appear in the ^{13}C-NMR spectrum at 55.3 and 51.7 ppm (MeO and MeN) and at 29.0 ppm for *Me*$_2$C. In the ^{1}H-NMR spectrum, MeO and MeN absorb both at 3.74 ppm, and the signal for Me_2C appears at 1.76 ppm. In the case of **13b**, the signals of the MeN and Me_2C groups are found at 3.72/49.4 and 1.86/30.7 ppm, respectively.

2. *Reaction of 2*H-*Azirin-3-amines* **1** *with* BF_3. The reaction of **1** (R^3 = Me, R^4 = Ar) with BF_3 in the absence of external nucleophiles was carried out by addition of an equimolar amount of $BF_3 \cdot OEt_2$ to a stirred solution of **1** in THF at −78°. The mixture was allowed to warm to room temperature and stirred for 12 h. After addition of Et_2O, solid products were filtered off and recrystallized, whereas oily materials were purified by chromatography (SiO_2; CH_2Cl_2/MeOH) to give 2-amino-1,3,3-trialkyl-3*H*-indolium tetrafluoroborates **14** in good yields [39] (*Scheme 5* and *Table 2*).

Scheme 5



1a - h **14**

Table 2. *Synthesized 3*H-*Indolium Tetrafluoroborates* **14** (yields in [%])

1	R^1	R^2	R	**14**
a	Me	$PhCH_2$	H	91
b	Me	Me_2CHCH_2	H	62
c	$-(CH_2)_3-$		H	84
d	$-(CH_2)_4-$		H	56
e	$-(CH_2)_5-$		H	59
f	$-(CH_2)_6-$		H	60
g	Me	Me	MeO	42
h	Me	Me	NO_2	26

The structures of the indolium tetrafluoroborates **14** formed have been established on the basis of spectroscopic data, elemental analyses, and, in the case of **14f**, by an X-ray crystal-structure determination. The IR spectra of the salts **14** show two characteristic absorption bands in the region of 3400–3200 cm^{-1} for N–H stretching vibrations of the NH_2 group, and an intense C=N absorption band at 1695–1680 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra were recorded mainly in (D_6)DMSO. In general, the ^{1}H-NMR spectra show two broad *singlets* for the NH_2 group and a *singlet* at 3.63–3.24 ppm for MeN. In the ^{13}C-NMR spectra, a *singlet* at 176.1–174.8 ppm for C(2) of the indole ring was observed. This signal is shifted upfield to 164.8 in **14c** and to 170.1 ppm in **14h**. Two signals at 56.3–46.8 (*s*) for C(3) and at 29.5–28.6 ppm (*q*) for MeN are shifted downfield to 61.2 and 45.2 for **14c**, and to 58.2 and 40.0 ppm for **14h**. The ^{1}H-NMR spectrum of **14b** in $CDCl_3$ shows that the H-atoms of the Me_2CHCH_2 group are not equivalent and appear at 2.38–2.28 and 2.09–2.00 ppm as an *ABX* system; the Me groups of the side chain absorb as *doublet*s at 0.73 and 0.55 ppm. The most-characteristic peak in the CI-MS of compounds **14** is that for $[M - BF_4]^+$, which, in general, is the base peak. The EI-MS of **14a**, **14b**, and **14d** give useful information about the fragmentation pattern of this class of compounds. In all cases, *m*/*z* 159 is a dominant peak.

The crystal structure of the spirocyclic **14f** is shown in *Fig. 1*. The indole ring system (N(1) to C(9)) is almost planar with C(10) and N(2) also being in this plane. In addition, the exocyclic NH_2 group is coplanar with the heterocyclic ring, and the short N(1),C(2) and N(2),C(2) bonds (1.326(2) and 1.310(2) Å, resp.) indicate a distinct π-conjugation in the amidinium moiety. On the other hand, the N(1),C(9) and N(2),C(2) bonds are normal single bonds (1.424(2) and 1.459(2) Å, resp.; see *Table 5*). Each H-atom of the NH_2 group of the cation forms an interionic H-bond with an F-atom of a neighboring BF_4^- anion in such a way that each cation interacts with two different acceptor anions that are related to each other by a crystallographic center of inversion. In turn, each anion, *via* two F-atoms, accepts two H-bonds, one being from each of two different centrosymmetrically related cations. The combination of these interactions links two cations and two anions into a closed tetrameric H-bonded loop with a graph set motif [40] of $R_4^4(12)$.

3. *Synthesis of Oxindoles and Related Compounds.* Treatment of aqueous solutions of **14** at 0° with aqueous NaOH (30%) and subsequent extraction with CH_2Cl_2 gave oily substances of type **15** in high yield, which, according to the spectroscopic data and, in the case of **15b**, elemental analysis, were either hydrates of 3,3-dialkyl-2,3-dihydro-1-

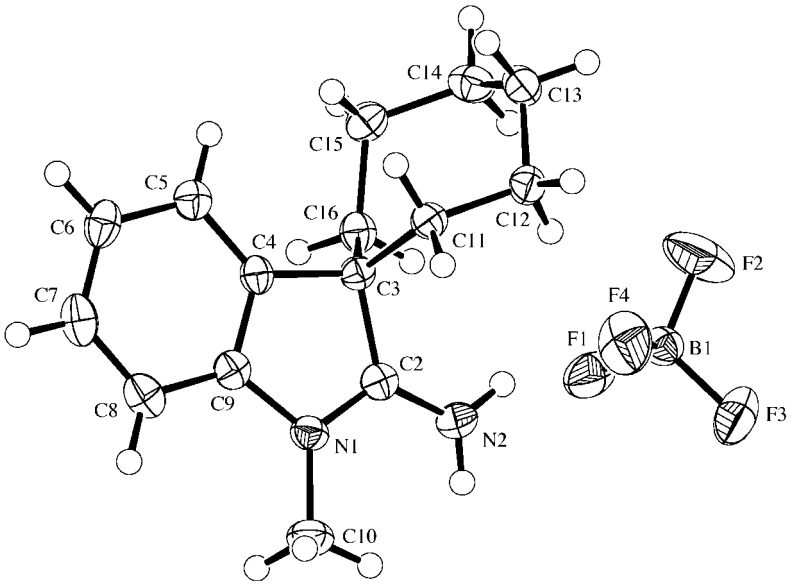


Fig. 1. *ORTEP Plot* [41] *of the molecular structure of* **14f** (arbitrary numbering of the atoms; 50% probability ellipsoids)

methyl-1*H*-indol-2-imines or the corresponding indolium hydroxides (*Scheme 6* and *Table 3*). In the IR spectra, the hydrates **15** show absorption bands in the region of 3305 – 3275 cm^{-1} for N–H stretching vibrations and an intense C=N band at 1651 – 1635 cm^{-1}. The CI-MS show the base peak for $[M+1-H_2O]^+$, whereas in the EI-MS a peak for $[M-H_2O]^+$ is observed. The ^{13}C-NMR spectra of compounds **15** are very similar to those of the corresponding tetrafluoroborates **14**.

Treatment of **14** with Ac_2O in pyridine at *ca.* 23° for 16 h followed by aqueous workup and chromatographic separation (SiO_2), yielded mixtures of *N*-(3,3-dialkyl-2,3-dihydro-1-methyl-1*H*-indol-2-yliden)acetamides **16** and 1,3-dihydro-2*H*-indol-2-ones (oxindoles) **17** (*Scheme 6* and *Table 3*).

Most likely, the initially formed *N*-acetyl derivative **16** was partly hydrolyzed under the workup conditions to give **17**. The latter could be obtained in good yield by the hydrolysis of **16** with aqueous HCl under reflux for 1 – 2 h. The hydrolysis of **16b** was carried out under milder conditions by stirring in 10% HCl solution at room temperature overnight to avoid the loss of the side chain[2]). It is worth mentioning that compounds **16** were also obtained from the hydrates **15** upon treatment with Ac_2O in pyridine. Furthermore, the oxindole derivatives **17** were accessible by hydrolysis of the hydrates **15** in H_2O/THF (*Scheme 6*). The yields of this hydrolysis as well as those of the *N*-acetyl derivatives **16** are listed in *Table 4*.

---

[2]) This undesired side reaction has been observed under more-drastic reaction conditions.

Scheme 6

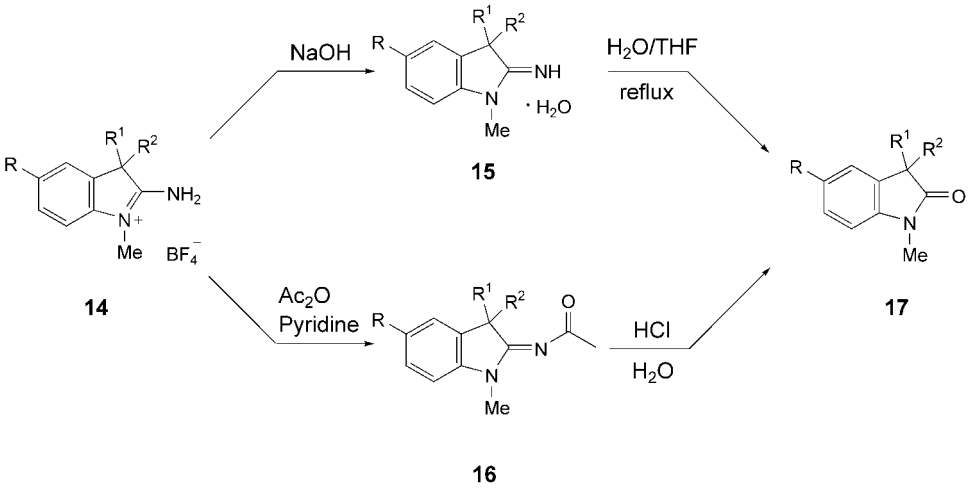


Table 3. *Synthesis of Hydrates* **15**, N-*Acetyl Derivatives* **16**, *and Oxindoles* **17** *from 3*H-*Indolium Tetrafluoroborates* **14** (yields in [%])

14	R^1	R^2	R	**15**	**16**	**17**
a	Me	$PhCH_2$	H	95	42	16
b	Me	Me_2CHCH_2	H	88	34	16
c	$-(CH_2)_3-$		H	94	–	53
d	$-(CH_2)_4-$		H	92	50	41
e	$-(CH_2)_5-$		H	96	57	32
f	$-(CH_2)_6-$		H	96	48	31
g	Me	Me	MeO	99	24	39
h	Me	Me	NO_2	–	29	5

Table 4. *Yields of Oxindoles* **17** [%] *from the Hydrolyses of* **15** (H_2O/THF) *and* **16** (aq. HCl)

17	R^1	R^2	R	From **15**	From **16**
a	Me	$PhCH_2$	H	92	88
b	Me	Me_2CHCH_2	H	94	80
c	$-(CH_2)_3-$		H	87	–
d	$-(CH_2)_4-$		H	94	94
e	$-(CH_2)_5-$		H	91	93
f	$-(CH_2)_6-$		H	89	86
g	Me	Me	MeO	95	89
h	Me	Me	NO_2	–	34

The IR spectra of the acetyl derivatives **16** show a characteristic group of three strong absorption bands at 1720 – 1665, 1660 – 1635, and 1615 – 1600 cm^{-1}. The first two correspond to C=O (amidic) and C=N stretching vibrations of the *N*-acetyl group, whereas the third band, together with another strong band at 1505 – 1490 cm^{-1}, indicates the aromatic nature of the compounds. In the ^{1}H-NMR spectra, characteristic

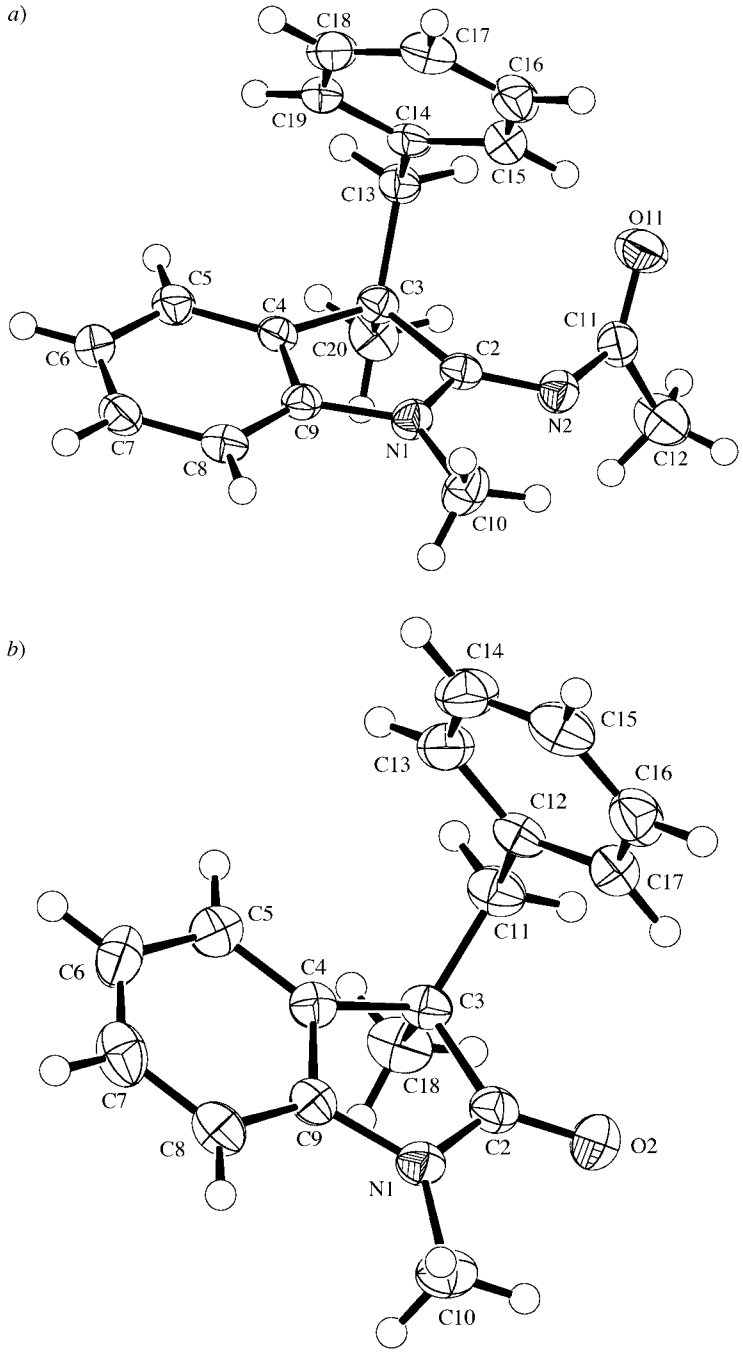


Fig. 2. *ORTEP Plots* [41] *of the molecular structures of* a) **16a** *and* b) **17a** (arbitrary numbering of the atoms; 50% probability ellipsoids)

signals are detected at 3.41 – 2.89 ppm for MeN and at 2.49 – 2.28 ppm for MeCO. In the ^{13}C-NMR spectra, characteristic *singlets* appear at 181.8 – 180.1 (C=O), 167.3 – 163.8 (C=N), and 56.1 – 46.4 ppm (C(3)). The CI-MS show the base peak at $[M+1]^+$. In the EI-MS fragmentation pattern of the acetyl derivative **16b**, a *McLafferty* rearrangement leads to the loss of isobutene to give a peak at *m/z* 202 (88). The base peak is at *m/z* 160. In addition, the structure of **16a** has been established by an X-ray crystal-structure determination (*Fig. 2*).

In the crystal structure of **16a**, the two fused rings are essentially planar, although C(2) deviates by 0.10 Å from the mean plane defined by the other eight ring atoms. As a result, the atoms of the substituent at C(2), namely N(2) and C(11), also deviate significantly from the ring plane. The C=O group is not coplanar with the C=N group, indicating a lack of conjugation between the C=O group and the amidine moiety of the molecule. For comparison, the C,N bond lengths of **16a** are listed in *Table 5*, together with those of the indolium tetrafluoroborate **14f** and the oxindole **17a**.

Table 5. *C–N Bond Lengths* [Å] *in the Crystal Structures of* **14f**, **16a**, *and* **17a**

C–N Bond	**14f**	**16a**	**17a**
N(1)–C(2)	1.326(2)	1.368(3)	1.370(3)
N(1)–C(9)	1.424(2)	1.407(2)	1.405(2)
N(1)–C(10)	1.459(2)	1.452(2)	1.452(3)
N(2)–C(2)	1.310(2)	1.284(2)	–
N(2)–C(11)	–	1.381(2)	–

The structures of the oxindoles of type **17** were also elucidated from spectroscopic data and elemental analyses. The IR spectra show strong absorptions at 1725 – 1700 cm^{-1} for amide C=O and at 1615 – 1600, 1496 – 1490 cm^{-1} for the aromatic ring. In the ^{1}H-NMR spectra ($CDCl_3$), the typical signals of the aromatic, alkyl, or spirocyclic part at C(3), and a characteristic *singlet* at 3.28 – 2.98 ppm for MeN are present. The ^{13}C-NMR spectra show two *singlets* at 182.3 – 179.8 (C=O) and 53.8 – 44.1 ppm (C(3)), and a *quadruplet* at 26.7 – 25.7 ppm for MeN. In the CI-MS (NH_3), the most-important peaks are $[M+NH_4]^+$ and $[M+1]^+$, whereas the EI-MS show the molecular ion ($M^{+\cdot}$) and *m/z* 160 as the base peak. Finally, the structure of **17a** has been established by a low-temperature X-ray crystal-structure determination (*Fig. 2*). The fused rings together with O(2) form a planar system. The C,N bond lengths involving N(1) are almost identical with those of the *N*-acetyl derivative **16a** (*Table 5*).

The mechanisms of the BF_3-catalyzed ring enlargement of 2*H*-azirin-3-amines **1** to indolium tetrafluoroborates and the subsequent transformation of the latter to oxindoles were discussed in [8].

We thank the analytical units of our institute for spectra and analyses. Financial support of this work by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

1. *General*. Solvents were purified by standard procedures. TLC: *Merck* TLC aluminium sheets, silica gel *60* F_{254}. Prep. TLC: *Merck* PLC plates (glass), silica gel *60* F_{254}, 2 mm. Column chromatography (CC): *Uetikon-Chemie* 'Chromatographiegel' *C-560*. M.p.: *Mettler-FP-5* apparatus or *Büchi 510* apparatus; uncorrected. IR

Spectra: *Perkin-Elmer-781* spectrophotometer or *Perkin-Elmer-1600-FT-IR* spectrophotometer; in cm^{-1}. ^1H-(300 MHz) and ^{13}C-NMR (75.5 MHz) Spectra: *Bruker ARX-300* instrument; at 300 K in $CDCl_3$, if not otherwise stated; δ in ppm, J in Hz; ^{13}C-signal multiplicity from DEPT spectra. MS: *Finnigan SSQ-700* or *MAT-90* instrument for CI (NH_3); *m/z* (rel. %).

Amides **6** and 2*H*-azirin-3-amines **1** reported in this paper were prepared according to known protocols. Only the syntheses of amides **6g** and **6h**, and the preparation of the new azirines **1g** and **1h** will be described.

2. *Synthesis of Amides* **6**. To a soln. of a 4-substituted *N*-methylaniline (1 equiv.) in dry dioxane containing Et_3N (1.2 equiv.), 2-methylpropanoyl chloride (1.2 equiv.) was added. The stirred mixture was heated under reflux for 2 h and left to cool to r.t. Then, the solvent was evaporated, and the residue was dissolved in $CHCl_3$, washed with aq. HCl (2%), sat. aq. $NaHCO_3$ soln., and brine, and dried (Na_2SO_4). The solvent was evaporated i.v., and the crude product was distilled or crystallized.

N-*(4-Methoxyphenyl)-2,*N-*dimethylpropanamide* (**6g**). 4-Methoxy-*N*-methylaniline (5 g, 36.4 mmol), dry dioxane (100 ml), Et_3N (6.1 ml, 43.8 mmol), and 2-methylpropanoyl chloride (4.62 ml, 43.8 mmol). Bulb-to-bulb distillation at $130°/2 \cdot 10^{-3}$ Torr yielded 7.25 g (96%) of **6g**. Pale yellow oil, which crystallized in h.v. IR (KBr): 3041*w*, 2969*s*, 2935*m*, 2874*m*, 2839*m*, 1652*s*, 1609*m*, 1584*m*, 1512*s*, 1470*s*, 1444*m*, 1423*m*, 1387*s*, 1361*m*, 1291*s*, 1269*s*, 1248*s*, 1182*m*, 1170*m*, 1119*s*, 1107*m*, 1093*m*, 1039*s*, 964*w*, 921*w*, 839*s*, 798*w*, 751*w*, 733*w*, 692*w*, 599*m*. ^1H-NMR: 7.10, 6.92 (*AA′BB′*, 4 arom. H); 3.83 (*s*, MeO); 3.22 (*s*, MeN); 2.57–2.45 (*m*, CH); 1.00 (*d*, $J = 7$, 2 Me). ^{13}C-NMR: 177.7 (*s*, C=O); 158.9, 137.1 (2*s*, 2 arom. C); 128.3, 114.9 (2*d*, 4 arom. CH); 55.5 (*q*, MeO); 37.6 (*q*, MeN); 30.9 (*d*, CH); 19.7 (*q*, 2 Me). CI-MS: 416 (14), 415 (49, $[2\,M+1]^+$), 209 (14), 208 (100, $[M+1]^+$), 207 (18, $M^{+\cdot}$), 137 (13).

*2,*N-*Dimethyl*-N-*(4-nitrophenyl)propanamide* (**6h**). *N*-Methyl-4-nitro-aniline (2.38 g, 15.6 mmol), dry dioxane (40 ml), Et_3N (2.6 ml, 18.7 mmol), and 2-methylpropanoyl chloride (2 ml, 18.9 mmol). Crystallization from hexane/Et_2O yielded 3.02 g (87%) of **6h**. Yellow solid. M.p. 103°. IR (KBr): 3107*w*, 3063*w*, 2967*m*, 2934*m*, 2872*w*, 1950*w*, 1662*s*, 1605*s*, 1592*s*, 1518*s*, 1496*s*, 1466*m*, 1421*m*, 1384*m*, 1343*s*, 1325*m*, 1298*s*, 1265*s*, 1171*w*, 1108*m*, 1092*m*, 1030*m*, 920*w*, 868*m*, 849*m*, 763*w*, 746*w*, 703*m*. ^1H-NMR: 8.20, 7.36 (*AA′BB′*, 4 arom. H); 3.24 (*s*, MeN); 2.61–2.46 (*m*, CH); 0.99 (*d*, $J = 6.7$, 2 Me). ^{13}C-NMR: 176.7 (*s*, C=O); 149.9, 146.1 (2*s*, 2 arom. C); 127.6, 124.8 (2*d*, 4 arom. CH); 37.2 (*q*, MeN); 31.2 (*d*, CH); 19.4 (*q*, 2 Me). EI-MS: 222 (1, $M^{+\cdot}$), 152 (5), 105 (4), 43 (100), 41 (28).

3. *Synthesis of 2,*N-*Dimethyl*-N-*(4-nitrophenyl)propanethioamide* (**12h**). To a soln. of **6h** (2.3 g, 10.35 mmol) in abs. toluene (23 ml) was added *Lawesson* reagent (2.3 g, 5.69 mmol), and the mixture was heated at 90° for 1 h. After cooling to r.t., the solvent was evaporated, and the crude product was purified by CC (AcOEt/hexane 3:10) to give 2.15 g (87%) of **12h**. Pale yellow powder. M.p. 149.0–149.6°. IR (KBr): 3100*w*, 3057*w*, 3035*w*, 2969*m*, 2928*m*, 2863*m*, 1608*s*, 1591*s*, 1528*s*, 1490*s*, 1451*s*, 1383*s*, 1349*s*, 1325*s*, 1310*s*, 1274*s*, 1204*m*, 1101*s*, 1034*s*, 1008*s*, 893*w*, 870*s*, 858*m*, 760*m*, 701*s*, 663*w*, 629*w*, 602*w*. ^1H-NMR: 8.35, 7.38 (*AA′BB′*, 4 arom. H); 3.73 (*s*, MeN); 2.91–2.75 (*m*, CH); 1.15 (*d*, $J = 6.5$, 2 Me). ^{13}C-NMR: 213.7 (*s*, C=S); 147.5, 145.2 (2*s*, 2 arom. C); 126.9, 125.4 (2*d*, 4 arom. CH); 45.3 (*q*, MeN); 38.8 (*d*, CH); 23.6 (*q*, 2 Me). CI-MS: 240 (13), 239 (100, $[M+1]^+$), 210 (6), 209 (46), 208 (9). Anal. calc. for $C_{11}H_{14}N_2O_2S$ (238.31): C 55.44, H 5.92, N 11.75, S 13.45; found: C 55.41, H 5.82, N 11.73, S 13.17.

4. *Synthesis of 2*H-*Azirin-3-amines. General Procedure 1* (*GP 1*). To a stirred soln. of $(i\text{-}Pr)_2NH$ (1.1 equiv.) in THF at −20°, BuLi (2M soln. in pentane, 1.1 equiv.) was added under Ar, and the mixture was allowed to warm to 0°. Then, a soln. of the corresponding amide **6** (1 equiv.) in 5 ml THF was added dropwise, the mixture was stirred at 0° for 1 h, and diphenyl phosphorochloridate (diphenoxyphosphoryl chloride, DPPCl; 1.03 equiv.) was added dropwise. After 30 min, the ice bath was removed, and the mixture was stirred for 24 h. The precipitate formed was removed by filtration under Ar, and the THF soln. was dropped into a suspension of NaN_3 (3 equiv.) in dry DMF. The mixture was stirred for 4 d at r.t. Then, Et_2O was added, the mixture was filtered over a *Celite* pad, the solvent was evaporated, and the residue was dissolved in Et_2O. The soln. was washed twice with 5% aq. $NaHCO_3$ soln., and the aq. layer was extracted with Et_2O. The combined org. layers were dried ($MgSO_4$), the solvent was evaporated i.v., and the crude product was purified by bulb-to-bulb distillation and/or CC.

4.1. N-*(4-Methoxyphenyl)-2,2,*N-*trimethyl-2*H-*azirin-3-amine* (**1g**). According to *GP 1*, with **6g** (3.43 g, 16.57 mmol), THF (83 ml), $(i\text{-}Pr)_2NH$ (2.7 ml, 19.05 mmol), BuLi (2M soln. in pentane, 9.2 ml, 18.4 mmol), DPPCl (3.5 ml, 17.06 mmol), NaN_3 (3.23, 49.68 mmol), and DMF (8.3 ml). Distillation at $110°/2 \cdot 10^{-3}$ Torr, followed by CC (AcOEt/hexane 1:2), yielded 2.93 g (87%) of **1g**. Slightly yellow oil. IR (film): 3050*m*, 2941*s*, 2836*s*, 1753*s*, 1649*m*, 1587*m*, 1512*s*, 1463*s*, 1370*s*, 1282*s*, 1248*s*, 1183*s*, 1125*s*, 1092*s*, 1033*s*, 950*s*, 825*s*, 791*m*, 773*m*, 677*w*, 654*w*, 639*m*, 610*s*. ^1H-NMR: 7.02, 6.91 (*AA′BB′*, 4 arom. H); 3.80 (*s*, MeO); 3.40 (*s*, MeN); 1.42 (*s*, 2 Me). ^{13}C-NMR: 155.8, 136.4 (2*s*, 2 arom. C); 117.9, 114.7 (2*d*, 4 arom. CH); 55.6 (*q*, MeO); 37.4 (*q*, MeN); 25.5 (*q*, 2

Me); C(2) and C(3) could not be detected. CI-MS: 206 (14), 205 (100, $[M+1]^+$), 138 (5). Anal. calc. for $C_{12}H_{16}N_2O$ (204.27): C 70.56, H 7.90, N 13.71; found: C 70.58, H 7.82, N 13.75.

4.2. *2,2,*N-*Trimethyl*-N-*(4-nitrophenyl)-2*H-*azirin-3-amine* (**1h**). 4.2.1. N-*(1-Chloro-2-methylprop-1-enyl)*-N-*methyl-4-nitrobenzenamine* (**11h**). To a stirred soln. of **12h** (4.74 g, 19.89 mmol) in abs. CH_2Cl_2 (77 ml) and 0.64 ml of DMF at 0° was added a soln. of $COCl_2$ in toluene (2N, 13 ml, 26 mmol). The mixture was stirred at 0° → r.t. for 1 h, the solvent was evaporated, the residue was dissolved in abs. THF (77 ml), and 1,4-diazabicyclo[2.2.2]octane (DABCO; 3.2 g, 28.53 mmol) was added. After stirring for 60 min at r.t., the mixture was filtered under N_2, the residue was washed with absolute THF, and the pale yellow soln. was evaporated. The chloro-enamine **11h** was obtained as a yellow oil. It was characterized and immediately used in the subsequent reaction.

Data of **11h**: IR (KBr): 3087*w*, 2995*w*, 2915*w*, 2825*w*, 2664*w*, 1595*s*, 1502*s*, 1470*m*, 1451*w*, 1315*s*, 1241*m*, 1189*m*, 1108*s*, 991*m*, 860*m*, 836*m*, 793*m*, 753*m*, 693*w*, 676*w*, 644*w*. ^{1}H-NMR: 8.12, 6.77 (*AA′BB′*, 4 arom. H); 3.15 (*s*, MeN); 1.94, 1.70 (2*s*, 2 Me). ^{13}C-NMR: 151.1, 139.7 (2*s*, 2 arom. C); 132.0 (*s*, =*C*Me$_2$); 128.5 (*s*, =CCl); 125.7, 112.5 (2*d*, 4 arom. CH); 37.2 (*q*, MeN); 20.6, 19.4 (2*q*, 2 Me). CI-MS: 261 (4), 260 (33, $[M+NH_4]^+$), 243 (10, $[M+1]^+$) for ^{37}Cl isotope, and 259 (13), 258 (100, $[M+NH_4]^+$), 241 (31, $[M+1]^+$) for ^{35}Cl isotope, 227 (5), 225 (16), 224 (7), 206 (6), 205 (44). Anal. calc. for $C_{11}H_{13}ClN_2O_2$ (240.69): C 54.89, H 5.44, N 11.64, Cl 14.73; found: C 54.99, H 5.51, N 11.96, Cl 14.22.

Compound **1h**: The chloro-enamine **11h** was dissolved in DMF (25 ml), NaN_3 (3.91 g, 60.39 mmol) was added, and the mixture was stirred at r.t. for 2 weeks. Then, it was filtered through a *Celite* pad, the column was washed with Et_2O, and the solvent was evaporated. The crude product was purified by CC (AcOEt/hexane 2:5): 2.46 g (56%) of **1h**. Yellow solid. M.p. 116.1–117.3°. IR (KBr): 3117*w*, 3075*w*, 2977*w*, 2948*m*, 2919*m*, 1742*s*, 1652*w*, 1599*s*, 1499*s*, 1451*s*, 1423*m*, 1391*m*, 1376*m*, 1314*s*, 1225*s*, 1184*m*, 1122*s*, 1110*s*, 946*m*, 837*s*, 752*s*, 688*m*, 628*m*. ^{1}H-NMR: 8.27 (*AA′BB′*, 2 arom. H); 7.31 (*m*, 2 arom. H); 3.52 (*s*, MeN); 1.49 (*s*, 2 Me). ^{13}C-NMR: 168.1 (*s*, C=N); 147.4, 142.6 (2*s*, 2 arom. C); 125.4, 115.1 (2*d*, 4 arom. CH); 25.2 (*q*, 2 Me); C(2) and MeN could not be detected. ESI-MS: 243 (14), 242 (100, $[M+Na]^+$), 220 (13, $[M+1]^+$). Anal. calc. for $C_{11}H_{13}N_3O_2$ (219.246): C 60.26, H 5.98, N 19.17; found: C 60.34, H 6.19, N 19.19.

5. *Reaction of 2*H-*Azirin-3-amines* **1** *with* $BF_3 \cdot OEt_2$. *General Procedure 2* (*GP 2*). To a stirred soln. of **1** (1 equiv.) in THF at −78°, $BF_3 \cdot OEt_2$ (*ca.* 48% BF_3 in Et_2O; 1.0–1.1 equiv.) was added. Then, the mixture was allowed to warm slowly to *ca.* 23° and was stirred for 12 h at this temp. After addition of Et_2O and filtration, the crude product was purified by crystallization or CC (SiO_2) to give **14**.

5.1. *2-Amino-3-benzyl-1,3-dimethyl-3*H-*indolium Tetrafluoroborate* (**14a**). According to *GP 2*, with **1a** (300 mg, 1.20 mmol), THF (30 ml), and $BF_3 \cdot OEt_2$ (0.32 ml, 1.22 mmol). CC (MeOH/CH_2Cl_2 1:10) yielded 370 mg (91%) of **14a.** Colorless viscous oil, which forms a foam in h.v. IR (film): 3379*s*, 3317*s*, 3246*s*, 3063*s*, 3033*s*, 2980*s*, 2937*s*, 2876*m*, 1694*s*, 1615*s*, 1496*s*, 1472*s*, 1455*s*, 1423*s*, 1385*m*, 1304*m*, 1047s, 916*w*, 843*w*, 761*s*, 726*m*, 703*s*. ^{1}H-NMR: 7.37 (br. *s*, NH_2); 7.32–7.15, 7.04–6.94, 6.88–6.83, 6.80–6.75 (4*m*, 9 arom. H); 3.25 (*s*, $PhCH_2$); 3.24 (*s*, MeN); 1.67 (*s*, Me). ^{13}C-NMR: 174.8 (*s*, C=N); 141.9, 134.0, 133.5 (3*s*, 3 arom. C); 129.5, 128.9, 127.8, 127.1, 124.9, 123.4, 110.0 (7*d*, 9 arom. CH); 52.9 (*s*, C(3)); 44.6 (*t*, $PhCH_2$); 28.6 (*q*, MeN); 22.3 (*q*, Me). EI-MS: 251 (6, $[M-BF_4]^+$), 250 (25), 160 (14), 159 (100), 144 (9), 143 (10), 134 (28), 117 (11), 91 (17), 77 (7). Anal. calc. for $C_{17}H_{19}BF_4N_2$ (338.15): C 60.38, H 5.66, N 8.28; found: C 60.39, H 5.77, N 7.99.

5.2. *2-Amino-1,3-dimethyl-3-(2-methylpropyl)-3*H-*indolium Tetrafluoroborate* (**14b**). According to *GP 2*, with **1b** (826 mg, 3.8 mmol), THF (83 ml), and $BF_3 \cdot OEt_2$ (1.0 ml, 3.8 mmol). CC (MeOH/CH_2Cl_2 0.5:10) yielded 720 mg (62%) of **14b**. Thick colorless oil, which gives a white solid in h.v. M.p. 156.5–157.5°. IR (KBr): 3391*m*, 3321*m*, 3256*s*, 3210*m*, 2963*s*, 2873*m*, 1683*s*, 1608*s*, 1504*m*, 1473*s*, 1423*m*, 1390*m*, 1368*w*, 1353*w*, 1306*m*, 1263*w*, 1242*w*, 1191*m*, 1084*s*, 937*w*, 837*w*, 766*s*, 756*s*, 699*w*. ^{1}H-NMR: 8.76, 8.52 (2 br. *s*, NH_2); 7.45–7.36, 7.32–7.25 (2*m*, 3 arom. H); 7.13 (*d*-like, 1 arom. H); 3.63 (*s*, MeN); 2.38–2.28, 2.09–2.00 (2*m*, CH_2); 1.61 (*s*, Me); 1.26–1.09 (*m*, CH); 0.73, 0.55 (2*d*-like, J = 6.6, 2 Me). ^{13}C-NMR: 176.1 (*s*, C=N); 141.6, 134.7 (2*s*, 2 arom. C); 128.8, 125.7, 122.9, 110.6 (4*d*, 4 arom. CH); 51.7 (*s*, C(3)); 46.3 (*t*, CH_2); 29.3 (*q*, MeN); 26.3 (*q*, Me); 25.4 (*d*, CH); 23.5, 22.7 (2*q*, 2 Me). EI-MS: 217 (4, $[M-BF_4]^+$), 216 (14), 173 (20), 161 (10), 160 (100), 159 (97), 144 (11), 130 (13), 117 (13), 106 (13), 100 (10). Anal. calc. for $C_{14}H_{21}BF_4N_2$ (304.13): C 55.29, H 6.96, N 9.21; found: C 55.51, H 6.84, N 9.10.

5.3. *2′-Amino-1′-methylspiro[cyclobutane-1,3′-[3*H*]indolium] Tetrafluoroborate* (**14c**). According to *GP 2*, with **1c** (555 mg, 2.98 mmol), THF (50 ml), and $BF_3 \cdot OEt_2$ (0.78 ml, 2.98 mmol). Filtration and washing of the precipitate with Et_2O yielded 686 mg (84%) of **14c**. White powder. M.p. 179.5–180.5°. IR (KBr): 3332*s*, 2966*m*, 1634*s*, 1591*s*, 1492*m*, 1456*s*, 1281*m*, 1063*s*, 854*w*, 778*m*, 703*s*, 604*w*. ^{1}H-NMR ((D_6)DMSO): 7.63–7.43 (*m*, 4 arom. H); 5.52 (br. *s*, NH_2); 3.51 (*s*, MeN); 2.35–2.25 (*t*-like, 4 H); 2.03–1.82, 1.48–1.31 (2*m*, 1 H each). ^{13}C-NMR ((D_6)DMSO): 164.8 (*s*, C=N); 143.8 (*s*, 1 arom. C); 130.0, 128.4, 125.8 (3*d*, 4 arom. CH); 61.2 (*s*, C(3)); 45.2 (*q*,

MeN); 35.5 (*t*, 2 CH_2); 14.1 (*t*, CH_2). CI-MS: 188 (10), 187 (100, $[M - BF_4]^+$), 172 (47), 171 (13), 108 (58), 107 (11). Anal. calc. for $C_{12}H_{15}N_2BF_4$ (274.07): C 52.59, H 5.52, N 10.22; found: C 52.48, H 5.68, N 10.10.

5.4. *2′-Amino-1′-methylspiro[cyclopentane-1,3′-[3*H*]indolium] Tetrafluoroborate* (**14d**). According to *GP 2*, with **1d** (629 mg, 3.14 mmol), THF (65 ml), and $BF_3 \cdot OEt_2$ (0.83 ml, 3.17 mmol). Filtration and washing of the precipitate with Et_2O yielded 510 mg (56%) of **14d**. White powder. M.p. 212–212.5°. IR (KBr): 3378*s*, 3313*m*, 3242*s*, 3215*s*, 3159*m*, 3064*m*, 2964*s*, 2884*m*, 1690*s*, 1611*s*, 1596*m*, 1505*m*, 1469*s*, 1459*s*, 1422*m*, 1355*m*, 1324*m*, 1299*m*, 1268*w*, 1149*s*, 1112*s*, 1041*s*, 1003*s*, 938*w*, 868*w*, 767*s*, 760*s*, 740*w*, 678*s*. ^{1}H-NMR ((D_6)DMSO): 9.78 (br. *s*, NH_2); 7.51–7.41 (*m*, 2 arom. H); 7.35 (*d*-like, 1 arom. H); 7.25 (*t*-like, 1 arom. H); 3.49 (*s*, MeN); 2.19–1.89 (*m*, 4 CH_2). ^{13}C-NMR ((D_6)DMSO): 175.7 (*s*, C=N); 141.3, 137.4 (2*s*, 2 arom. C); 128.1, 125.1, 122.4, 110.5 (4*d*, 4 arom. CH); 56.3 (*s*, C(3)); 39.1, 25.5 (2*t*, 4 CH_2); 29.4 (*q*, MeN). EI-MS: 201 (4, $[M - BF_4]^+$), 200 (12), 160 (9), 159 (100), 144 (12). Anal. calc. for $C_{13}H_{17}BF_4N_2$ (288.09): C 54.20, H 5.95, N 9.72; found: C 53.96, H 5.96, N 9.54.

5.5. *2′-Amino-1′-methylspiro[cyclohexane-1,3′-[3*H*]indolium] Tetrafluoroborate* (**14e**). According to *GP 2*, with **1e** (619 mg, 2.89 mmol), THF (62 ml), and $BF_3 \cdot OEt_2$ (0.84 ml, 3.21 mmol). Crystallization from EtOH yielded 514 mg (59%) of **14e**. White powder. M.p. 246.5–247.5°. IR (KBr): 3389*s*, 3256*s*, 2942*s*, 2865*s*, 1682*s*, 1607*s*, 1505*s*, 1469*s*, 1350*s*, 1311*s*, 1272*m*, 1048*s*, 936*m*, 847*w*, 750*s*, 692*m*. ^{1}H-NMR ((D_6)DMSO): 9.95, 9.74 (2 br. *s*, NH_2); 7.84 (*d*-like, 1 arom. H); 7.48 (*t*-like, 1 arom. H); 7.37 (*d*-like, 1 arom. H); 7.23 (*t*-like, 1 arom. H); 3.49 (*s*, MeN); 1.98–1.75, 1.65–1.56 (2*m*, 5 CH_2). ^{13}C-NMR ((D_6)DMSO): 175.1 (*s*, C=N); 141.8, 134.6 (2*s*, 2 arom. C); 128.4, 125.1, 124.3, 111.0 (4*d*, 4 arom. CH); 50.3 (*s*, C(3)); 32.4, 23.9, 20.3 (3*t*, 5 CH_2); 29.5 (*q*, MeN). CI-MS: 216 (16), 215 (100, $[M - BF_4]^+$). Anal. calc. for $C_{14}H_{19}BF_4N_2$ (302.12): C 55.66, H 6.34, N 9.27; found: C 55.39, H 6.38, N 9.20.

5.6. *2′-Amino-1′-methylspiro[cycloheptane-1,3′-[3*H*]indolium] Tetrafluoroborate* (**14f**). According to *GP 2*, with **1f** (263 mg, 1.15 mmol), THF (26 ml), and $BF_3 \cdot OEt_2$ (0.32 ml, 1.22 mmol). Crystallization from EtOH yielded 220 mg (60%) of **14f**. Colorless needles. M.p. 237.5–238.5°. Crystals suitable for an X-ray crystal-structure determination were grown from EtOH. IR (KBr): 3392*s*, 3320*m*, 3254*s*, 2990*m*, 2929*s*, 2863*m*, 1686*s*, 1609*s*, 1501*m*, 1468*s*, 1425*m*, 1351*m*, 1322*w*, 1301*w*, 1271*w*, 1060*s*, 970*m*, 872*w*, 758*s*, 687*w*. ^{1}H-NMR ((D_6)DMSO): 9.70 (br. *s*, NH_2); 7.68 (*d*-like, 1 arom. H); 7.44 (*t*-like, 1 arom. H); 7.35 (*d*-like, 1 arom. H); 7.25 (*t*-like, 1 arom. H); 3.48 (*s*, MeN); 2.07–1.71 (*m*, 6 CH_2). ^{13}C-NMR ((D_6)DMSO): 176.0 (*s*, C=N); 141.4, 136.2 (2*s*, 2 arom. C); 128.4, 124.8, 123.7, 110.9 (4*d*, 4 arom. CH); 53.6 (*s*, C(3)); 36.3, 29.2, 22.9 (3*t*, 6 CH_2); 29.4 (*q*, MeN). CI-MS: 230 (16), 229 (100, $[M - BF_4]^+$), 218 (28), 108 (21). Anal. calc. for $C_{15}H_{21}BF_4N_2$ (316.15): C 56.99, H 6.70, N 8.86; found: C 56.78, H 6.66, N 8.63.

5.7. *2-Amino-5-methoxy-1,3,3-trimethyl-3*H*-indolium Tetrafluoroborate* (**14g**). According to *GP 2*, with **1g** (628 mg, 3.07 mmol), THF (80ml), and $BF_3 \cdot OEt_2$ (0.92 ml, 3.52 mmol). Filtration and washing of the precipitate with Et_2O yielded 379 mg (42%) of **14g**. White solid, which was recrystallized from EtOH to give colorless crystals. M.p. 253.8–254.2°. IR (KBr): 3386*s*, 3316*m*, 3251*s*, 3218*s*, 3008*m*, 2844*w*, 1688*s*, 1612*s*, 1504*s*, 1484*s*, 1463*s*, 1447*m*, 1291*s*, 1255*m*, 1217*s*, 1028*s*, 884*m*, 820*s*, 767*w*, 656*m*. ^{1}H-NMR ((D_6)DMSO): 9.89, 9.57 (2 br. *s*, 2 NH); 7.30–7.18 (*m*, 2 arom. H); 7.00–6.92 (*m*, 1 arom. H); 3.76 (*s*, MeO); 3.47 (*s*, MeN); 1.51 (*s*, 2 Me). ^{13}C-NMR ((D_6)DMSO): 175.0 (*s*, C=N); 157.4, 137.5, 134.8 (3*s*, 3 arom. C); 113.0, 111.4, 109.4 (3*d*, 3 arom. CH); 55.7 (*q*, MeO); 47.1 (*s*, C(3)); 29.4 (*q*, MeN); 24.1 (*q*, 2 Me). CI-MS: 410 (11, $[2\,M - BF_4]^+$), 409 (40, $[2\,M - BF_4 - 1]^+$), 206 (14), 205 (100, $[M - BF_4]^+$). Anal. calc. for $C_{12}H_{17}BF_4N_2O$ (292.08): C 49.35, H 5.87, N 9.59; found: C 49.45, H 5.81, N 9.61.

5.8. *2-Amino-1,3,3-trimethyl-5-nitro-3*H*-indolium Tetrafluoroborate* (**14h**). According to *GP 2*, with **1h** (1.85 g, 8.44 mmol), THF (185 ml), and $BF_3 \cdot OEt_2$ (2.463 ml, 9.41 mmol). Filtration and washing of the precipitate with Et_2O yielded 681 mg (26%) of **14h**. Pale yellow solid. M.p. 211–213°. IR (KBr): 3366*m*, 3222*s*, 3114*m*, 3081*m*, 2997*m*, 1690*s*, 1641*s*, 1592*s*, 1522*s*, 1387*s*, 1347*s*, 1297*m*, 1246*m*, 1193*m*, 1061*s*, 916*s*, 873*m*, 855*m*, 833*w*, 789*w*, 756*w*, 723*w*, 705*m*. ^{1}H-NMR ((D_6)DMSO): 8.34 (*d*-like, 1 arom. H); 8.18 (br. *s*, 1 arom. H); 7.71 (*d*-like, 1 arom. H); 3.32 (*s*, MeN); 1.37 (*s*, 2 Me). ^{13}C-NMR ((D_6)-DMSO): 170.1 (s, C=N); 148.8, 146.6, 137.3 (3*s*, 3 arom. C); 129.6, 124.8, 111.3 (3*d*, 3 arom. CH); 58.2 (*s*, C(3)); 40.0 (*q*, MeN); 23.9 (*q*, 2 Me). CI-MS: 238 (100), 222 (9), 221 (9), 220 (71, $[M - BF_4]^+$), 190 (7).

6. *Reaction of 3*H*-Indolium Tetrafluoroborates* **14** *with NaOH. General Procedure 3* (*GP 3*). A soln. of **14** in the least amount of H_2O was cooled to 0°, and aq. NaOH (30%) was added. The cooled mixture (ice bath) was stirred for 25 min to 2 h. After extraction with CH_2Cl_2, the org. phase was washed with brine and dried (Na_2SO_4). Evaporation of the solvent gave **15**.

6.1. *3-Benzyl-1,3-dihydro-2-imino-1,3-dimethyl-2*H*-indole Hydrate* (**15a**). According to *GP 3*, with **14a** (328 mg, 0.70 mmol), 30% aq. NaOH (3.5 ml), stirring for 2 h. Yield: 248 mg (95%) of **15a**. Pale yellow, viscous oil. IR (film): 3304*m*, 3058*m*, 3030*m*, 2963*m*, 2924*m*, 1645*s*, 1608*s*, 1573*s*, 1496*s*, 1468*s*, 1452*s*, 1389*s*, 1363*m*, 1308*m*, 1265*w*, 1227*m*, 1191*m*, 1157*w*, 1122*m*, 1097*s*, 1075*w*, 1055*w*, 1031*w*, 1020*m*, 995*s*, 922*w*, 856*w*, 749*s*, 699*s*,

663*w*, 622*w*. ^{1}H-NMR: 7.17–7.00 (*m*, 6 arom. H); 6.90–6.81 (*m*, 3 arom. H); 3.00 (*s*, MeN); 2.93 (*s*, $PhCH_2$); 1.42 (*s*, Me). ^{13}C-NMR: 174.8 (*s*, C=N); 145.0, 135.9, 133.3 (*s*, 3 arom. C); 130.0, 129.8, 128.1, 128.0, 127.8, 126.4, 122.9, 120.2, 106.4 (9*d*, 9 arom. CH); 49.7 (*s*, C(3)); 46.6 (*t*, $PhCH_2$); 26.6 (*q*, MeN); 24.4 (*q*, Me). CI-MS: 252 (18), 251 (100, $[M+1-H_2O]^+$).

6.2. *1,3-Dihydro-2-imino-1,3-dimethyl-3-(2-methylpropyl)-2*H-*indole Hydrate* (**15b**). According to *GP 3*, with **14b** (25 mg, 0.08 mmol), 30% aq. NaOH (2.5 ml), stirring for 25 min. Yield: 17 mg (88%) of **15b**. Colorless viscous oil. IR (film): 3305*m*, 3054*m*, 2958*s*, 2870*m*, 1647*s*, 1608*s*, 1496*s*, 1468*s*, 1388*m*, 1363*m*, 1309*m*, 1262*m*, 1210*m*, 1125*s*, 1086*m*, 1046*m*, 1020*m*, 999*m*, 978*m*, 918*w*, 746*s*, 699*w*, 622*w*. ^{1}H-NMR: 7.16 (*t*-like, 1 arom. H); 7.03 (*d*-like, 1 arom. H); 6.89 (*t*-like, 1 arom. H); 6.70 (*d*-like, 1 arom. H); 5.55 (br. *s*, NH); 3.27 (*s*, MeN); 1.79–1.71 (*m*, CH_2); 1.28 (*s*, Me); 1.22–1.12 (*m*, CH); 0.60, 0.47 (2*d*-like, $J = 6.7$, 2 Me). ^{13}C-NMR: 176.1 (*s*, C=N); 144.7, 134.4 (2*s*, 2 arom. C); 127.7, 122.5, 121.1, 107.1 (4*d*, 4 arom. CH); 48.8 (*s*, C(3)); 48.3 (*t*, CH_2); 28.1 (*q*, MeN); 27.5 (*q*, Me); 25.4 (*d*, CH); 23.8, 23.3 (2*q*, 2 Me). GC/EI-MS: 216 (11, $[M-H_2O]^{+\bullet}$), 173 (19), 160 (100), 159 (77), 144 (12), 130 (9), 117 (12), 77 (5). Anal. calc. for $C_{14}H_{22}N_2O$ (234.34): C 71.76, H 9.46, N 11.95; found: C 72.00, H 9.29, N 11.76.

6.3. *1′,3′-Dihydro-2′-imino-1′-methylspiro[cyclobutane-1,3′-[2*H*]indole] Hydrate* (**15c**). According to *GP 3*, with **14c** (100 mg, 0.36 mmol), 30% aq. NaOH (10 ml), stirring for 2 h. Yield: 70 mg (94%) of **15c**. Pale yellow viscous oil. IR (film): 3302*m*, 2948*s*, 1651*s*, 1600*s*, 1494*s*, 1388*s*, 1345*s*, 1273*s*, 1230*s*, 1160*s*, 1125*s*, 1054*m*, 1020*m*, 983*s*, 847*m*, 748*s*, 701*s*, 605*w*. ^{1}H-NMR ((D_6)DMSO): 7.33 (*t*-like, 2 arom. H); 7.08 (*t*-like, 1 arom. H); 6.92 (*d*-like, 1 arom. H); 3.20 (*s*, MeN); 2.33–2.21 (*m*, 2 H); 2.05–1.88 (*m*, 1 H); 1.82–1.70 (*m*, 2 H); 1.50–1.35 (*m*, 1 H). ^{13}C-NMR ((D_6)DMSO): 168.1 (*s*, C=N); 148.5 (*s*, 1 arom. C); 129.2, 123.3, 122.2 (3*d*, 4 arom. CH); 63.7 (*s*, C(3)); 42.3 (*q*, MeN); 37.0 (*t*, 2 CH_2); 15.4 (*t*, CH_2). CI-MS: 188 (18), 187 (100, $[M+1-H_2O]^+$).

6.4. *1′,3′-Dihydro-2′-imino-1′-methylspiro[cyclopentane-1,3′-[2*H*]indole] Hydrate* (**15d**). According to *GP 3*, with **14d** (50 mg, 0.17 mmol), 30% aq. NaOH (5 ml), stirring for 2 h. CC ($MeOH/CH_2Cl_2$ 1.5:10) yielded 35 mg (92%) of **15d**. Colorless viscous oil. IR (film): 3302*m*, 3053*m*, 2955*s*, 2870*m*, 1645*s*, 1607*s*, 1495*s*, 1467*s*, 1428*m*, 1387*s*, 1362*m*, 1301*m*, 1272*w*, 1216*m*, 1179*w*, 1158*w*, 1141*m*, 1124*m*, 1097*m*, 1065*m*, 1022*m*, 962*s*, 922*w*, 849*w*, 743*s*, 693*w*. ^{1}H-NMR ((D_6)DMSO): 7.20–7.15 (*m*, 2 arom. H); 6.87 (*t*-like, 1 arom. H); 6.82 (*d*-like, 1 arom. H); 3.65 (br. *s*, NH); 3.14 (*s*, MeN); 2.02–1.85, 1.81–1.67 (*m*, 4 CH_2). ^{1}H-NMR: 7.13 (*t*-like, 1 arom. H); 7.07 (*d*-like, 1 arom. H); 6.85 (*t*-like, 1 arom. H); 6.63 (*d*-like, 1 arom. H); 5.07 (br. *s*, NH); 3.18 (*s*, MeN); 2.00–1.82 (2*m*, 4 CH_2). ^{13}C-NMR ((D_6)DMSO): 174.9 (*s*, C=N); 144.3, 137.0 (2*s*, 2 arom. C); 127.3, 121.8, 120.4, 106.5 (4*d*, 4 arom. CH); 53.8 (*s*, C(3)); 40.3, 25.7 (2*t*, 4 CH_2); 26.8 (*q*, MeN). ^{13}C-NMR: 177.8 (*s*, C=N); 144.5, 137.4 (2*s*, 2 arom. C); 127.4, 121.9, 120.8, 106.5 (4*d*, 4 arom. CH); 54.7 (*s*, C(3)); 41.0, 26.5 (2*t*, 4 CH_2); 26.5 (*q*, MeN). GC/EI-MS: 201 (2, $[M+1-H_2O]^+$), 200 (14, $[M-H_2O]^{+\bullet}$), 160 (13), 159 (100), 144 (6).

6.5. *1′,3′-Dihydro-2′-imino-1′-methylspiro[cyclohexane-1,3′-[2*H*]indole] Hydrate* (**15e**). According to *GP 3*, with **14e** (64 mg, 0.21 mmol), 30% aq. NaOH (6.4 ml), stirring for 2 h. Yield: 47 mg (96%) of **15e**. Colorless oil, which solidified at 0°. IR (KBr): 3278*s*, 3055*m*, 2931*s*, 2854*s*, 1635*s*, 1603*s*, 1496*s*, 1466*s*, 1449*s*, 1393*s*, 1364*m*, 1311*s*, 1298*m*, 1228*s*, 1187*m*, 1159*m*, 1124*s*, 1074*m*, 1028*m*, 995*s*, 935*m*, 916*m*, 853*m*, 817*m*, 793*m*, 759*m*, 742*s*, 693*m*, 674*w*. ^{1}H-NMR ((D_6)DMSO): 7.73 (*d*-like, 1 arom. H); 7.42 (*t*-like, 1 arom. H); 7.11–7.02 (*m*, 2 arom. H); 3.32 (*s*, MeN); 2.07–1.87, 1.80–1.54 (2*m*, 5 CH_2). ^{13}C-NMR ((D_6)DMSO): 173.8 (*s*, C=N); 144.6, 134.7 (2*s*, 2 arom. C); 127.3, 124.0, 119.4, 106.5 (4*d*, 4 arom. CH); 46.9 (*s*, C(3)); 34.6, 24.5, 20.8 (3*t*, 5 CH_2); 26.6 (*q*, MeN). CI-MS: 216 (16), 215 (100, $[M+1-H_2O]^+$).

6.6. *1′,3′-Dihydro-2′-imino-1′-methylspiro[cycloheptane-1,3′-[2*H*]indole] Hydrate* (**15f**). According to *GP 3*, with **14f** (60 mg, 0.19 mmol), 30% aq. NaOH (6.0 ml), stirring for 2 h. Yield: 45 mg (96%) of **15f**. Pale yellow viscous oil. IR (film): 3323*m*, 3051*m*, 2923*s*, 2852*s*, 1644*s*, 1604*s*, 1494*s*, 1464*s*, 1386*s*, 1358*m*, 1307*m*, 1264*m*, 1216*m*, 1160*m*, 1123*m*, 1081*m*, 1045*m*, 1025*m*, 1008*m*, 990*s*, 961*w*, 741*s*, 690*m*. ^{1}H-NMR ((D_6)DMSO): 7.32 (*d*-like, 1 arom. H); 7.16 (*t*-like, 1 arom. H); 6.85 (*t*-like, 1 arom. H); 6.78 (*d*-like, 1 arom. H); 3.09 (*s*, MeN); 1.90–1.55 (*m*, 6 CH_2). ^{13}C-NMR ((D_6)DMSO): 175.2 (*s*, C=N); 144.2, 137.0 (2*s*, 2 arom. C); 127.3, 122.4, 119.8, 106.5 (4*d*, 4 arom. CH); 50.0 (*s*, C(3)); 26.5 (*q*, MeN); 38.7, 30.5, 23.2 (3*t*, 6 CH_2). CI-MS: 230 (17, $[M-OH+1]^+$), 229 (100, $[M-OH]^+$ or $[M-NH_3]^{+\bullet}$).

6.7. *1,3-Dihydro-2-imino-5-methoxy-1,3,3-trimethyl-2*H-*indole Hydrate* (**15g**). According to *GP 3*, with **14g** (61.5 mg, 0.21 mmol), 30 % aq. NaOH (6 ml), stirring for 2 h. Yield: 46.5 mg (99%) of **15g**. Colorless viscous oil. IR (film): 3304*m*, 3035*m*, 2963*s*, 2929*s*, 2865*m*, 2834*m*, 1645*s*, 1599*s*, 1503s, 1471*s*, 1437*s*, 1388*s*, 1363*m*, 1290*s*, 1242*s*, 1213*s*, 1182*m*, 1114*s*, 1068*m*, 1032*s*, 1005*s*, 946*m*, 909*w*, 874*m*, 853*s*, 801*s*, 715*w*, 695*m*, 615*w*, 603*m*. ^{1}H-NMR ((D_6)DMSO): 6.91–6.89, 6.78–6.68 (2*m*, 3 arom. H); 3.70 (*s*, MeO); 3.09 (*s*, MeN); 1.27 (*s*, 2 Me). ^{13}C-NMR ((D_6)DMSO): 174.7 (*s*, C=N); 154.1, 138.3, 137.1 (3*s*, 3 arom. C); 111.7, 109.8, 106.5 (3*d*, 3 arom. CH); 55.5 (*q*, MeO); 44.0 (*s*, C(3)); 26.6 (*q*, MeN); 26.2 (*q*, 2 Me). CI-MS: 206 (15), 205 (100, $[M+1-H_2O]^+$).

7. *Reaction of 3*H-*Indolium Tetrafluoroborates* **14** *with* Ac_2O/*Pyridine. General Procedure 4* (*GP 4*). A soln. of **14** in pyridine/Ac_2O 1:1 (*v*/*v*) was stirred at *ca.* 23° for 16 h. Then, the solvent was evaporated, and the residue was dissolved in $CHCl_3$, washed with H_2O and brine, and dried (Na_2SO_4). After filtration, evaporation, and CC with the proper solvent mixture, two products **16** and **17** were isolated.

7.1. N-*(3-Benzyl-1,3-dihydro-1,3-dimethyl-2*H-*indol-2-yliden)acetamide* (**16a**) *and 3-Benzyl-1,3-dihydro-1,3-dimethyl-2*H-*indol-2-one* (**17a**). According to *GP 4*, with **14a** (647 mg, 1.91 mmol), pyridine/Ac_2O (6.5 ml each), CC (Et_2O/hexane 2:5). The two products were purified by means of HPLC (AcOEt/hexane 2:10, 0.5 ml/min, 13 atm). Crystallization of the main product from hexane yielded 233 mg (42%) of **16a**. Colorless prisms. M.p. 99.7°. Crystals suitable for an X-ray crystal-structure determination were grown from hexane. IR (KBr): 3052*w*, 2964*w*, 2926*w*, 1669*s*, 1639*s*, 1603*s*, 1494*s*, 1470*m*, 1379*m*, 1354*m*, 1288*m*, 1224*s*, 1209*m*, 1199*s*, 1154*w*, 1125*m*, 1102*m*, 1079*w*, 1062*m*, 1025*w*, 998*w*, 952*m*, 943*m*, 807*w*, 764*m*, 748*m*, 710*s*, 675*w*, 650*w*, 602*m*. ^{1}H-NMR: 7.21–6.98 (*m*, 6 arom. H); 6.91–6.84 (*m*, 2 arom. H); 6.54 (*d*-like, 1 arom. H); 3.53, 3.01 (*AB*, J = 12.7, PhCH_2); 2.89 (*s*, MeN); 2.33 (*s*, MeCO); 1.58 (*s*, Me). ^{13}C-NMR: 181.7 (*s*, C=O); 165.1 (*s*, C=N); 143.7, 136.2, 134.2 (3*s*, 3 arom. C); 129.7, 127.8, 127.2, 126.2, 122.5, 121.8, 107.5 (7*d*, 9 arom. CH); 52.3 (*s*, C(3)); 46.8 (*t*, PhCH$_2$); 28.1, 27.5 (2*q*, *Me*CO, MeN); 22.4 (*q*, Me). CI-MS: 294 (16), 293 (100, $[M+1]^+$). Anal. calc. for $C_{19}H_{20}N_2O$ (292.37): C 78.05, H 6.89, N 9.58; found: C 78.07, H 7.04, N 9.57.

As a minor product, 79 mg (16%) of **17a** was obtained. Crystallization from hexane gave colorless prisms suitable for an X-ray crystal-structure determination. M.p. 96.5° ([42]: 89–94°). IR (KBr): 3058*w*, 3029*w*, 2971*m*, 2922*m*, 1703*s*, 1613*s*, 1496*s*, 1473*m*, 1449*s*, 1422*w*, 1377*s*, 1350*m*, 1266*m*, 1245*w*, 1124*m*, 1103*m*, 1086*w*, 1053*w*, 1026*m*, 941*w*, 913*w*, 757*s*, 738*m*, 701*s*, 604*w*. ^{1}H-NMR: 7.21–7.02 (*m*, 6 arom. H); 6.88–6.83 (*m*, 2 arom. H); 6.64–6.59 (*d*-like, 1 arom. H); 3.11, 3.00 (*AB*, J = 13, PhCH$_2$); 2.98 (*s*, MeN); 1.48 (*s*, Me). ^{13}C-NMR: 179.8 (*s*, C=O); 143.1, 136.1, 132.9 (3*s*, 3 arom. C); 129.7, 127.6, 127.4, 126.3, 123.2, 121.9, 107.6 (7*d*, 9 arom. CH); 49.8 (*s*, C(3)); 44.5 (*t*, PhCH$_2$); 25.7 (*q*, MeN); 22.6 (*q*, Me). CI-MS: 270 (5), 269 (32, $[M+NH_4]^+$), 253 (18), 252 (100, $[M+1]^+$). Anal. calc. for $C_{17}H_{17}NO$ (251.32): C 81.24, H 6.82, N 5.57; found: C 81.29, H 6.70, N 5.56.

7.2. N-*[1,3-Dihydro-1,3-dimethyl-3-(2-methylpropyl)-2*H-*indol-2-yliden]acetamide* (**16b**) *and 1,3-Dihydro-1,3-dimethyl-3-(2-methylpropyl)-2*H-*indol-2-one* (**17b**). According to *GP 4*, with **14b** (300 mg, 0.99 mmol), pyridine/Ac_2O (3 ml each). CC (Et_2O/hexane 3:10) yielded 863 mg (34%) of **16b**. Colorless oil. IR (film): 3055*w*, 2957*s*, 2928*s*, 2870*m*, 1651*s*, 1603*s*, 1493*s*, 1470*s*, 1432*s*, 1378*s*, 1352*s*, 1290*s*, 1211*s*, 1158*m*, 1133*s*, 1091*s*, 1061*w*, 1021*m*, 999*m*, 978*m*, 944*s*, 885*w*, 855*w*, 804*w*, 749*s*, 716*w*, 654*m*, 600*s*. ^{1}H-NMR: 7.45 (*t*-like, 1 arom. H); 7.30 (*d*-like, 1 arom. H); 7.22 (*t*-like, 1 arom. H); 7.00 (*d*-like, 1 arom. H); 3.41 (*s*, MeN); 2.49 (*s*, MeCO); 2.32–2.22, 1.99–1.90 (2*m*, CH$_2$); 1.68 (*s*, Me); 1.61–1.44 (*m*, CH); 0.96, 0.70 (*2d*, 2 Me). ^{13}C-NMR: 181.1 (*s*, C=O); 165.6 (*s*, C=N); 143.6, 135.6 (2*s*, 2 arom. C); 127.6, 122.2, 122.0, 107.8 (4*d*, 4 arom. CH); 50.6 (*s*, C(3)); 47.7 (*t*, CH$_2$); 28.6, 27.3 (2*q*, *Me*CO, MeN); 27.6 (*q*, Me); 25.7 (*d*, CH); 23.5, 23.2 (*2q*, 2 Me). EI-MS: 258 (13, $M^{+\bullet}$), 243 (8), 215 (35), 202 (88), 187 (7), 173 (30), 160 (100), 159 (70), 158 (12), 144 (17), 132 (10), 117 (12). Anal. calc. for $C_{16}H_{22}N_2O$ (258.36): C 74.38, H 8.58, N 10.84; found: C 74.10, H 8.71, N 10.61.

As a minor product, 34 mg (16%) of **17b** was obtained. Colorless oil. IR (film): 3055*m*, 2958*s*, 2870*s*, 1719*s*, 1613*s*, 1493*s*, 1471*s*, 1452*s*, 1423*m*, 1377*s*, 1347*s*, 1309*m*, 1250*m*, 1174*m*, 1157*w*, 1126*s*, 1086*s*, 1050*m*, 1024*s*, 981*w*, 920*w*, 753*s*, 741*s*, 699*m*, 640*w*. ^{1}H-NMR: 7.28 (*t*-like, 1 arom. H); 7.15 (*d*-like, 1 arom. H); 7.07 (*t*-like, 1 arom. H); 6.85 (*d*-like, 1 arom. H); 3.22 (*s*, MeN); 2.00–1.92, 1.80–1.72 (2*m*, CH$_2$); 1.32 (*s*, Me); 1.31–1.18 (*m*, CH); 0.65, 0.61 (*2d*, 2 Me). ^{13}C-NMR: 180.9 (*s*, C=O); 143.1, 134.1 (2*s*, 2 arom. C); 127.4, 122.7, 122.2, 107.8 (4*d*, 4 arom. CH); 47.9 (*s*, C(3)); 46.7 (*t*, CH$_2$); 26.0 (*q*, MeN); 25.4 (*d*, CH); 24.0 (*q*, Me); 22.7 (*q*, 2 Me). GC/EI-MS: 217 (10, $M^{+\bullet}$), 162 (11), 161 (100), 160 (57), 130 (13), 117 (10). Anal. calc. for $C_{14}H_{19}NO$ (217.31): C 77.38, H 8.81, N 6.45; found: C 77.08, H 8.76, N 6.41.

7.3. N-*(1′,3′-Dihydro-1′-methylspiro[cyclobutane-1,3′-[2*H*]indol]-2′-yliden)acetamide* (**16c**) *and 1′,3′-Dihydro-1′-methylspiro[cyclobutane-1,3′-[2*H*]indol]-2′-one* (**17c**). According to *GP 4*, with **14c** (200 mg, 0.73 mmol), pyridine/Ac_2O (2 ml each). CC (Et_2O/hexane 2:5) yielded 73 mg (53%) of **17c**. Colorless oil. The acetamide **16c** could not be isolated, but was identified by EI-GC/MS.

Data of **17c**: IR (film): 3567*w*, 3055*m*, 2987*m*, 2936*s*, 2884*m*, 1713*s*, 1614*s*, 1493*s*, 1470*s*, 1423*m*, 1375*s*, 1349*s*, 1313*m*, 1273*m*, 1250*m*, 1165*m*, 1120*m*, 1100*s*, 1062*m*, 1007*m*, 942*w*, 750*s*, 698*m*. ^{1}H-NMR: 7.53–7.47 (*d*-like, 1 arom. H); 7.30–7.22 (*t*-like, 1 arom. H); 7.12–7.05 (*t*-like, 1 arom. H); 6.8–6.76 (*d*-like, 1 arom. H); 3.19 (*s*, MeN); 2.70–2.61 (*m*, CH$_2$); 2.41–2.24 (*m*, 2 CH$_2$). ^{13}C-NMR: 180.1 (*s*, C=O); 142.9, 134.3 (2*s*, 2 arom. C); 127.7, 122.4, 122.1, 107.5 (4*d*, 4 arom. CH); 48.0 (*s*, C(3)); 31.2 (*t*, 2 CH$_2$); 26.0 (*q*, MeN); 16.6 (*t*, CH$_2$). GC/EI-MS: 188 (3), 187 (33, $M^{+\bullet}$), 160 (10), 159 (100), 131 (24), 130 (39), 115 (4), 103 (7), 89 (9), 77 (10). Anal. calc. for $C_{12}H_{13}NO$ (187.24): C 76.98, H 7.00, N 7.48; found: C 76.91, H 7.03, N 7.46.

7.4. N-*(1′,3′-Dihydro-1′-methylspiro[cyclopentane-1,3′-[2*H*]indol]-2′-yliden)acetamide* (**16d**) *and 1′,3′-Dihydro-1′-methylspiro[cyclopentane-1,3′-[2*H*]indol]-2′-one* (**17d**). According to *GP 4*, with **14d** (200 mg,

0.69 mmol), pyridine/Ac_2O (2 ml each). CC (AcOEt/hexane 1:5) yielded 84 mg (50%) of **16d**. Colorless oil. IR (film): 3054*w*, 2955*s*, 2871*m*, 1711*s*, 1651*s*, 1604*s*, 1492*s*, 1470*s*, 1428*m*, 1376*s*, 1352*s*, 1292*m*, 1281*m*, 1211*s*, 1170*m*, 1126*m*, 1086*s*, 1023*m*, 965*s*, 925*w*, 853*w*, 800*w*, 746*s*, 697*w*, 655*w*, 600*m*. ^{1}H-NMR: 7.28–7.15 (*m*, 2 arom. H); 7.03 (*t*-like, 1 arom. H); 6.80 (*d*-like, 1 arom. H); 3.20 (*s*, MeN); 2.43–2.32, 2.09–1.80 (2*m*, 4 CH_2); 2.28 (*s*, MeCO). ^{13}C-NMR: 180.8 (*s*, C=O); 167.3 (*s*, C=N); 142.9, 138.9 (2*s*, 2 arom. C); 127.3, 122.4, 121.8, 107.7 (4*d*, 4 arom. CH); 56.1 (*s*, C(3)); 39.8, 26.6 (2*t*, 4 CH_2); 29.2, 27.3 (2*q*, *Me*CO, MeN). GC/EI-MS: 243 (3), 242 (23, $M^{+\cdot}$), 227 (11), 214 (22), 202 (8), 201 (79), 160 (100), 159 (60), 130 (38), 115 (13).

As a minor product, 57 mg (41%) of **17d** was obtained. Colorless oil, which solidified in h.v. to give a white solid. M.p. 58.7° ([43]: 58–59°). IR (KBr): 3054*w*, 2955*m*, 2870*w*, 1711*s*, 1613*s*, 1493*s*, 1470*s*, 1421*w*, 1376*s*, 1348*s*, 1317*w*, 1301*w*, 1264*w*, 1159*w*, 1124*m*, 1094*w*, 1078*m*, 1021*w*, 969*w*, 746*m*, 697*w*. ^{1}H-NMR: 7.28–7.15 (*m*, 1 arom. H); 7.04 (*t*-like, 1 arom. H); 6.81 (*d*-like, 1 arom. H); 3.20 (*s*, MeN); 2.21–1.92, 1.87–1.78 (2*m*, 4 CH_2). ^{13}C-NMR: 181.8 (*s*, C=O); 142.8, 136.7 (2*s*, 2 arom. C); 127.2, 122.4, 122.1, 107.6 (4*d*, 4 arom. CH); 53.8 (*s*, C(3)); 38.2, 26.5 (2*t*, 4 CH_2); 26.1 (*q*, MeN). GC/EI-MS: 202 (4), 201 (33, $M^{+\cdot}$), 161 (12), 160 (100), 159 (13), 144 (6), 130 (17). Anal. calc. for $C_{13}H_{15}NO$ (201.27): C 77.58, H 7.51, N 6.96; found: C 77.28, H 7.28, N 6.92.

7.5. N-*(1′,3′-Dihydro-1′-methylspiro[cyclohexane-1,3′-[2*H*]indol]-2-yliden)acetamide* (**13e**) *and 1′,3′-Dihydro-1′-methylspiro[cyclohexane-1,3′-[2*H*]indol]-2′-one* (**17e**). According to *GP 4*, with **14e** (152 mg, 0.50 mmol), pyridine/Ac_2O (1.5 ml each). CC (AcOEt/hexane 1:2) yielded 73 mg (57%) of **16e**. Slightly yellow oil. IR (film): 3054*w*, 2934*s*, 2866*m*, 1711–1652*s* (br.), 1604*s* 1490*s*, 1470*s*, 1376*s*, 1353*s*, 1302*m*, 1283*s*, 1217*s*, 1161*w*, 1144*w*, 1126*m*, 1100*m*, 1085*s*, 1029*m*, 993*m*, 939*s*, 908*w*, 861*w*, 746*s*, 694*m*, 600*m*. ^{1}H-NMR: 7.56 (*d*-like, 1 arom. H); 7.29 (*t*-like, 1 arom. H); 7.02 (*t*-like, 1 arom. H); 6.85 (*d*-like, 1 arom. H); 3.17 (*s*, MeN); 2.28 (*s*, MeCO); 2.10–1.97, 1.89–1.75, 1.67–1.57 (3*m*, 5 CH_2). ^{13}C-NMR: 180.1 (*s*, C=O); 165.6 (*s*, C=N); 143.5, 135.8 (2*s*, 2 arom. C); 127.5, 124.4, 121.7, 108.1 (4*d*, 4 arom. CH); 49.9 (*s*, C(3)); 33.7, 24.7, 21.1 (3*t*, 5 CH_2); 29.7, 27.3 (2*q*, *Me*CO, MeN). CI-MS: 258 (18), 257 (100, $[M+1]^+$), 216 (34).

As a minor product, 57 mg (32%) of **17e** was obtained. Colorless viscous oil (*cf.* [44]). IR (film): 3054*w*, 2933*s*, 2854*s*, 1712*s*, 1645*m*, 1612*s*, 1493*s*, 1470*s*, 1449*s*, 1421*m*, 1377*s*, 1351*s*, 1313*m*, 1295*m*, 1252*s*, 1161*m*, 1144*m*, 1122*m*, 1092*m*, 1081*m*, 1066*m*, 1027*m*, 1007*m*, 935*m*, 912*w*, 857*w*, 757*s*, 745*s*, 694*m*. ^{1}H-NMR: 7.45 (*d*-like, 1 arom. H); 7.30 (*t*-like, 1 arom. H); 7.07 (*t*-like, 1 arom. H); 6.85 (*d*-like, 1 arom. H); 3.21 (*s*, MeN); 2.01–1.51 (*m*, 5 CH_2). ^{13}C-NMR: 180.6 (*s*, C=O); 142.7, 135.3 (2*s*, 2 arom. C); 127.3, 123.7, 121.8, 107.7 (4*d*, 4 arom. CH); 47.4 (*s*, C(3)); 32.9, 25.1, 21.1 (3*t*, 5 CH_2); 26.0 (*q*, MeN). CI-MS: 217 (16), 216 (100, $[M+1]^+$), 215 (12, $M^{+\cdot}$).

The reaction described above was also carried out with hydrate **15e** as the starting material: **15e** (144 mg, 0.62 mmol), pyridine/Ac_2O (1.5 ml each). CC (AcOEt/hexane 1:2) yielded 98.5 mg (62%) of **16e** and 21.6 mg (16%) of **17e**.

7.6. N-*(1′,3′-Dihydro-1′-methylspiro[cycloheptane-1,3′-[2*H*]indol]-2′-yliden)acetamide* (**16f**) *and 1′,3′-Dihydro-1′-methylspiro[cycloheptane-1,3′-[2*H*]indol]-2′-one* (**17f**). According to *GP 4*, with **14f** (110 mg, 0.35 mmol), pyridine/Ac_2O (1.1 ml each). CC (AcOEt/hexane 1:2) yielded 45 mg (48%) of **16f**. Slightly yellow oil. IR (film): 3054*m*, 2923*s*, 2855*s*, 1711–1651*s* (br.), 1604*s* 1490*s*, 1463*s*, 1351*s*, 1292*s*, 1275*s*, 1245*s*, 1212*s*, 1167*m*, 1130*m*, 1113*m*, 1092*s*, 1028*m*, 1013*m*, 992*m*, 963*s*, 915*m*, 892*m*, 856*w*, 803*w*, 744*s*, 723*m*, 693*m*, 651*w*, 600*s*. ^{1}H-NMR: 7.38 (*d*-like, 1 arom. H); 7.25 (*t*-like, 1 arom. H); 7.05 (*t*-like, 1 arom. H); 6.81 (*d*-like, 1 arom. H); 3.15 (*s*, MeN); 2.28 (*s*, MeCO); 2.19–2.05, 1.98–1.83, 1.82–1.58 (3*m*, 6 CH_2). ^{13}C-NMR: 180.1 (*s*, C=O); 165.5 (*s*, C=N); 143.2, 137.9 (2*s*, 2 arom. C); 127.5, 123.1, 122.3, 108.0 (4*d*, 4 arom. CH); 52.5 (*s*, C(3)); 30.0, 27.1 (2*q*, *Me*CO, MeN); 38.1, 31.0, 24.0 (3*t*, 6 CH_2). CI-MS: 272 (16), 271 (100, $[M+1]^+$), 230 (27), 210 (23), 196 (15), 134 (5), 122 (9).

As a minor product, 24.5 mg (31%) of **17f** was obtained. Colorless oil. IR (film): 3054*m*, 2923*s*, 2854*s*, 1714*s*, 1612*s*, 1494*s*, 1471*s*, 1420*m*, 1377*s*, 1346*s*, 1307*m*, 1282*w*, 1258*s*, 1238*m*, 1170*m*, 1125*s*, 1112*m*, 1082*s*, 1025*m*, 1012*m*, 965*s*, 926*w*, 904*w*, 883*w*, 857*w*, 744*s*, 693*m*, 652*w*. ^{1}H-NMR: 7.35 (*d*-like, 1 arom. H); 7.25 (*t*-like, 1 arom. H); 7.04 (*t*-like, 1 arom. H); 6.81 (*d*-like, 1 arom. H); 3.18 (*s*, MeN); 2.05–1.91, 1.83–1.65 (2*m*, 6 CH_2). ^{13}C-NMR: 182.3 (*s*, C=O); 142.5, 137.3 (2*s*, 2 arom. C); 127.2, 122.6, 122.2, 107.7 (4*d*, 4 arom. CH); 50.0 (*s*, C(3)); 36.8, 31.1, 23.7 (3*t*, 6 CH_2); 26.0 (*q*, MeN). CI-MS: 231 (16), 230 (100, $[M+1]^+$).

7.7. N-*(1,3-Dihydro-5-methoxy-1,3,3-trimethyl-2*H*-indol-2-yliden)acetamide* (**16g**) *and 1,3-Dihydro-5-methoxy-1,3,3-trimethyl-2*H*-indole-2-one* (**17g**). According to *GP 4*, with **14g** (151.5 mg, 0.52 mmol), pyridine/Ac_2O (1.5 ml each). CC (AcOEt/hexane 3.5:10) yielded 30.2 mg (24%) of **16g**. Pale yellow oil. IR (film): 2968*s*, 2931*s*, 2836*m*, 1709*s*, 1650*s*, 1502*s*, 1437*s*, 1383*s*, 1356*s*, 1305*s*, 1281*s*, 1213*s*, 1125*s*, 1058*s*, 1028*s*, 1002*m*, 949*s*, 925*m*, 909*m*, 878*s*, 803*s*, 729*s*, 692*w*, 645*w*, 627*w*, 600*m*. ^{1}H-NMR: 6.83–6.69 (*m*, 3 arom. H); 3.81 (*s*, MeO); 3.20 (*s*, MeN); 2.28 (*s*, MeCO); 1.51 (*s*, 2 Me). ^{13}C-NMR: 181.0 (*s*, C=O); 165.2 (*s*, C=N); 156.0, 138.6, 136.2 (3*s*, 3 arom. C); 111.8, 109.3, 108.1 (3*d*, 3 arom. CH); 55.7 (*q*, MeO); 47.2 (*s*, C(3)); 28.7, 27.3 (2*q*, *Me*CO, MeN); 25.9

(*q*, 2 Me). CI-MS: 247 (19, $[M+1]^+$), 206 (100), 77 (19). Anal. calc. for $C_{14}H_{18}N_2O_2$ (246.30): C 68.27, H 7.37, N 11.37; found: C 68.12, H 7.36, N 11.21.

As a second product, 41.1 mg (39%) of **17g** was obtained. Colorless viscous oil. (*cf.* [44]). IR (film): 3061*m*, 2967*s*, 2835*m*, 1714*s*, 1603*s*, 1494*s*, 1383*s*, 1355*s*, 1290*s*, 1246*s*, 1217*s*, 1180*s*, 1120*s*, 1067*s*, 1049*s*, 1028*s*, 946*m*, 882*s*, 869*m*, 805*s*, 754*w*, 744*m*, 729*m*, 697*s*, 624*m*, 612*m*. ^{1}H-NMR: 6.95–6.70 (*m*, 3 arom. H); 3.80 (*s*, MeO); 3.20 (*s*, MeN); 1.36 (*s*, 2 Me). ^{13}C-NMR: 181.0 (*s*, C=O); 156.1, 137.3, 136.2 (3*s*, 3 arom. C); 111.7, 110.1, 108.2 (3*d*, 3 arom. CH); 55.9 (*q*, MeO); 44.6 (*s*, C(3)); 26.3 (*q*, MeN); 24.4 (*q*, 2 Me). CI-MS: 411 (17, $[2\,M+1]^+$), 207 (14), 206 (100, $[M+1]^+$), 205 (13, $M^{+\bullet}$). Anal. calc. for $C_{12}H_{15}NO_2$ (205.25): C 70.22, H 7.37, N 6.82; found: C 70.06, H 7.39, N 6.84.

7.8. N-*(1,3-Dihydro-1,3,3-trimethyl-5-nitro-2*H*-indol-2-yliden)acetamide* (**16h**) *and 1,3-dihydro-1,3,3-trimethyl-5-nitro-2*H*-indole-2-one* (**17h**). According to *GP 4*, with **14h** (172.2 mg, 0.56 mmol), pyridine/Ac_2O (1.7 ml each). CC (AcOEt/hexane 1:2) yielded 42.8 mg (29%) of **16h**. Yellow powder. M.p. 136.4–138.2°. IR (KBr): 3086*w*, 2968*w*, 2929*m*, 1729*m*, 1695*s*, 1658*s*, 1610*s*, 1498*s*, 1466*m*, 1439*m*, 1390*m*, 1332*s*, 1263*s*, 1202*s*, 1123*s*, 1058*s*, 1031*m*, 1002*m*, 949*s*, 885*w*, 835*w*, 825*m*, 797*m*, 758*m*, 737*m*, 703*w*, 677*m*. ^{1}H-NMR: 8.22, 8.01, 6.85 (3*d*-like, 3 arom. H); 3.26 (*s*, MeN); 2.32 (*s*, MeCO); 1.58 (*s*, 2 Me). ^{13}C-NMR: 181.7 (*s*, C=O); 163.8 (*s*, C=N); 148.7, 142.8, 137.4 (3*s*, 3 arom. C); 125.4, 117.6, 107.0 (3*d*, 3 arom. CH); 46.4 (*s*, C(3)); 28.3, 27.2 (2*q*, *Me*CO, MeN); 25.7 (*q*, 2 Me). CI-MS: 263 (15), 262 (100, $[M+1]^+$), 238 (12), 232 (26), 210 (12). EI-MS: 261 (47, $M^{+\bullet}$), 246 (100), 231 (18), 218 (12), 204 (24).

As a minor product, 6.4 mg (5%) of **17h** was obtained. Yellow solid. M.p. 202.3–203.3° ([45]: 204–205°). IR (KBr): 3109*w*, 2977*w*, 2928*w*, 1725*s*, 1615*s*, 1509*s*, 1492*s*, 1463*m*, 1434*w*, 1416*m*, 1390*m*, 1378*m*, 1351*s*, 1332*s*, 1295*s*, 1266*m*, 1237*m*, 1195*w*, 1132*m*, 1119*s*, 1104*m*, 1049*m*, 1040*s*, 942*m*, 895*m*, 836*m*, 794*w*, 757*m*, 737*w*, 710*w*, 662*w*. ^{1}H-NMR: 8.25, 8.09, 6.92 (3*d*-like, 3 arom. H); 3.28 (*s*, MeN); 1.44 (*s*, 2 Me). ^{13}C-NMR: 181.3 (*s*, C=O); 148.4, 143.8, 136.5 (3*s*, 3 arom. C); 125.2, 118.3, 107.6 (3*d*, 3 arom. CH); 44.2 (*s*, C(3)); 26.7 (*q*, MeN); 24.2 (*q*, 2 Me). GC/EI-MS: 221 (13), 220 (100, $M^{+\bullet}$), 206 (10), 205 (80), 190 (10), 174 (10), 159 (37), 130 (23). CI-MS: 239 (13), 238 (100, $[M+NH_4]^+$), 221 (11, $[M+1]^+$), 220 (7, $M^{+\bullet}$), 192 (6), 191 (47).

8. *Hydrolysis of Compounds* **15** *and* **16**. *General Procedure 5* (*GP 5*). A soln. of **15** in H_2O/THF 1:1 (*v*/*v*) was heated to reflux for up to several days and then extracted with Et_2O. The org. phase was washed with brine and dried (Na_2SO_4). Evaporation of the solvent, followed by CC, gave **17**. *General Procedure 6* (*GP 6*). A soln. of **16** in aq. HCl (10%) was either heated to reflux for 1–2 h or stirred at r.t. overnight and then extracted with Et_2O. The org. phase was washed with aq. $NaHCO_3$ soln., and brine, and dried (Na_2SO_4). Evaporation of the solvent, followed by CC, gave **17**.

8.1. *Hydrolysis of* **15a** *and* **16a**. According to *GP 5*, with **15a** (126 mg, 0.47 mmol) and H_2O/THF (19 ml each). Heating to reflux for 2 d yielded 109 mg (92%) of **17a**. According to *GP 6*, with **16a** (20 mg, 0.07 mmol) and 10% aq. HCl (2 ml). Heating to reflux for 2 h gave 15.2 mg (88%) of **17a**.

8.2. *Hydrolysis of* **15b** *and* **16b**. According to *GP 5*, with **15b** (15 mg, 0.06 mmol) and H_2O/THF (2.5 ml each). Heating to reflux for 2 d yielded 13 mg (94%) of **17b**. According to *GP 6*, with **16b** (80 mg, 0.31 mmol) and 10% aq. HCl (8 ml). Stirring at r.t overnight. CC (Et_2O/hexane 3:10) yielded 54 mg (80%) of **17b**.

8.3. *Hydrolysis of* **15c**. According to *GP 5*, with **15c** (30 mg, 0.15 mmol) and H_2O/THF (4.5 ml each). Heating to reflux for 2 d yielded 23.8 mg (87%) of **17c**.

8.4. *Hydrolysis of* **15d** *and* **16d**. According to *GP 5*, with **15d** (45 mg, 0.47 mmol) and H_2O/THF (7 ml each). Heating to reflux for 2 d yielded 39 mg (94%) of **17d**. According to *GP 6*, with **16d** (50 mg, 0.21 mmol) and 10% aq. HCl (5 ml). Heating to reflux for 1 h yielded 39 mg (94%) of **17d**.

8.5. *Hydrolysis of* **15e** *and* **16e**. According to *GP 5*, with **15e** (15.5 mg, 0.07 mmol) and H_2O/THF (1.5 ml each). Heating to reflux for 3 d yielded 13 mg (91%) of **17e**. According to *GP 6*, with **16e** (50 mg, 0.20 mmol) and 10% aq. HCl (5 ml). Heating to reflux for 1 h gave 39 mg (93%) of **17e**.

8.6. *Hydrolysis of* **15f** *and* **16f**. According to *GP 5*, with **15f** (16 mg, 0.07 mmol) and H_2O/THF (2 ml each). Heating to reflux for 3 d yielded 13.3 mg (89%) of **17f**. According to *GP 6*, with **16f** (20 mg, 0.07 mmol) and 10% aq. HCl (2 ml). Heating to reflux for 1 h gave 14.6 mg (86%) of **17f**.

8.7. *Hydrolysis of* **15g** *and* **16g**. According to *GP 5*, with **15g** (20 mg, 0.07 mmol) and H_2O/THF (3 ml each). Heating to reflux for 3 d yielded 13.34 mg (95%) of **17g**. According to *GP 6*, with **16g** (20 mg, 0.08 mmol) and 10% aq. HCl (2 ml). Heating to reflux for 1 h gave 14.9 mg (89%) of **17g**.

8.8. *Hydrolysis of* **16h**. According to *GP 6*, with **16h** (14 mg, 0.054 mmol) and 10% aq. HCl (2 ml). Heating to reflux for 1 h yielded 4 mg (34%) of **17h**.

9. *Reaction of 2*H*-Azirin-3-amines* **1g** *and* **1h** *with Thiobenzoic* S*-Acid. General Procedure 7* (*GP 7*). To a well stirred soln. of thiobenzoic *S*-acid (1 equiv.) in abs. MeCN at 0°, a soln. of the corresponding azirine **1** (1 equiv.) in MeCN was added. The soln. was allowed to warm to r.t. and was stirred overnight. Then, the solvent

was evaporated, the residue was dissolved in CH_2Cl_2, and the org. phase was washed with sat. $NaHCO_3$ and brine, and dried (Na_2SO_4). Pure product was obtained after CC.

9.1. N-*{1,1-Dimethyl-2-[(4-methoxyphenyl)(methyl)amino]-2-thioxoethyl}benzamide* (**13a**). With thiobenzoic *S*-acid (43.5, 0.31 mmol) in 1.5 ml of MeCN and **1g** (64.3 mg, 0.31 mmol) in 0.6 ml of MeCN. CC (MeOH/CH_2Cl_2 0.1:10) yielded 93.1 mg (88%) of **13a**. White solid. M.p. 158.2–159.3°. IR (KBr): 3258*s*, 3061*m*, 3003*m*, 2935*w*, 2836*w*, 1637*s*, 1605*m*, 1579*m*, 1543*s*, 1501*s*, 1463*s*, 1431*m*, 1385*s*, 1369*s*, 1321*s*, 1291*s*, 1251*s*, 1213*w*, 1178*m*, 1165*m*, 1108*s*, 1096*s*, 1076*m*, 1033*m*, 994*m*, 940*w*, 930*w*, 920*w*, 844*m*, 819*w*, 804*w*, 760*w*, 724*s*, 695*m*, 670*w*, 635*w*, 621*w*. ^{1}H-NMR: 7.68 (*AA′*BB′, 2 arom. H); 7.43–7.34 (*m*, 3 arom. H); 7.12 (AA′*BB′*, 2 arom. H); 6.75 (*d*-like, 2 arom. H); 3.74 (*s*, MeO, MeN); 1.76 (*s*, 2 Me). ^{13}C-NMR: 209.1 (*s*, C=S); 165.0 (*s*, C=O); 159.0, 139.8, 135.1 (3*s*, 3 arom. C); 131.1, 128.4, 127.2, 126.8, 114.4 (5*d*, 9 arom. CH); 62.8 (*s*, Me_2C); 55.3, 51.7 (2*q*, MeO, MeN); 29.0 (*q*, 2 Me). CI-MS: 344 (36), 343 (79, $[M+1]^+$), 289 (10), 242 (11), 222 (100), 139 (60).

9.2. N-*{1,1-Dimethyl-2-[(methyl)(4-nitrophenyl)amino]-2-thioxoethyl}benzamide* (**13b**). With thiobenzoic *S*-acid (56 mg, 0.41 mmol) in 2 ml of MeCN and **8h** (90 mg, 41 mmol) in 0.7 ml of MeCN. CC (AcOEt/hexane 2:5) yielded 135 mg (92%) of **13b**. Bright yellow solid. M.p. 150.5–151.3°. IR (KBr): 3293*m*, 3104*w*, 3064*m*, 2989*w*, 2930*w*, 1642*s*, 1606*m*, 1591*s*, 1524*s*, 1489*s*, 1456*s*, 1433*s*, 1388*s*, 1346*s*, 1310*s*, 1260*m*, 1215*m*, 1172*m*, 1100*s*, 1027*m*, 1015*m*, 998*w*, 928*w*, 912*w*, 866*m*, 851*m*, 802*m*, 761*w*, 723*m*, 706*s*, 694*m*, 652*m*, 616*w*. ^{1}H-NMR: 8.08, 7.55 (*AA′BB′*, 4 arom. H); 7.45–7.35 (*m*, 5 arom. H); 6.62 (br. *s*, NH); 3.72 (*s*, MeN); 1.86 (*s*, 2 Me). ^{13}C-NMR: 209.4 (*s*, C=S); 165.4 (*s*, C=O); 153.5, 146.5, 133.8 (3*s*, 3 arom. C); 131.8, 128.4, 126.9, 126.6, 124.9 (5*d*, 9 arom. CH); 62.8 (*s*, Me_2C); 49.4 (*q*, MeN); 30.7 (*q*, 2 Me). CI-MS: 359 (23), 358 (100, $[M+1]^+$), 342 (12), 341 (10), 340 (47),

Table 6. *Crystallographic Data of Compounds* **14f**, **16a**, *and* **17a**

	14f	**16a**	**17a**
Crystallized from	EtOH	hexane	hexane
Empirical formula	$C_{15}H_{21}BF_4N_2$	$C_{19}H_{20}N_2O$	$C_{17}H_{17}NO$
Formula weight [g mol^{-1}]	316.15	292.38	251.33
Crystal color, habit	colorless, needle	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.05 × 0.10 × 0.25	0.28 × 0.33 × 0.48	0.25 × 0.30 × 0.38
Temp. [K]	160(1)	173(1)	173(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
Z	4	4	8
Reflections for cell determination	3649	25	25
2θ Range for cell determination [°]	4–55	36–40	36–40
Unit-cell parameters a [Å]	6.5212(1)	9.708(2)	14.014(5)
b [Å]	11.7323(2)	16.472(2)	12.895(5)
c [Å]	19.8657(5)	10.947(1)	15.863(4)
β [°]	94.1542(8)	114.283(9)	108.01(2)
V [Å^3]	1515.91(5)	1595.7(4)	2726(2)
D_x [g cm^3]	1.385	1.217	1.225
μ(MoK_α) [mm^{-1}]	0.115	0.0758	0.0757
Scan type	ϕ and ω	$\omega/2\theta$	$\omega/2\theta$
2θ(max) [°]	55	55	55
Total reflections measured	30898	4012	3404
Symmetry-independent reflections	3479	3666	3133
Reflections used [$I > 2\sigma(I)$]	2540	2634	1995
Parameters refined	207	200	173
Final R	0.0491	0.0471	0.0472
wR	0.0504	0.0458	0.0402
Goodness-of-fit	3.097	1.968	1.909
Secondary extinction coefficient	–	$2.3(1) \times 10^{-6}$	$4.2(4) \times 10^{-7}$
Final Δ_{max}/σ	0.0004	0.0002	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]	0.33; −0.26	0.24; −0.28	0.22; −0.24

324 (8), 323 (7), 312 (6), 311 (31), 223 (25). Anal. calc. for $C_{18}H_{19}N_3O_3S$ (357.43): C 60.49, H 5.36, N 11.76, S 8.97; found: C 60.27, H 5.63, N 11.75, S 8.68.

10. *X-Ray Crystal-Structure Determination of* **14f**, **16a**, *and* **17a** (see *Table 6*, and *Figs. 1* and *2*)[3]). All measurements were conducted using graphite-monochromated MoK_α radiation (λ 0.71073 Å) on a *Rigaku AFC5R* diffractometer fitted to a 12-kW rotating-anode generator (**16a** and **17a**) or on a *Nonius KappaCCD* area-detector diffractometer [46] equipped with an *Oxford Cryosystems Cryostream 700* cooler (**14f**). The data collection and refinement parameters are given in *Table 6*, and views of the molecules are shown in *Figs. 1* and *2*. Data reduction for **14f** was performed with *HKL Denzo* and *Scalepack* [47]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Each structure was solved by direct methods using SIR92 (**14f** and **17a**) [48] or SHELXS97 (**16a**) [49], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The amine H-atoms of **14f** were placed in the positions indicated by a difference-electron-density map, and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms of **14f** and all H-atoms of **16a** and **17a** were placed in geometrically calculated positions, and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom. Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$. A correction for secondary extinction was applied in the cases of **16a** and **17a**. For **14f**, three reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral-atom-scattering factors for non-H-atoms were taken from [50a], and the scattering factors for H-atoms were taken from [51]. Anomalous dispersion effects were included in F_c [52]; the values for f' and f'' were those of [50b]. The values of the mass attenuation coefficients are those of [50c]. All calculations were performed using the teXsan crystallographic software package [53].

REFERENCES

[1] R. J. Sundberg, 'Indoles', Academic Press, New York, 1996, p. 5.
[2] B. Robinson, 'The Fischer Indole Synthesis', John Wiley, Chichester, 1982.
[3] G. Baccolini, P. E. Todesco, *J. Chem. Soc., Chem. Commun.* **1981**, 563.
[4] M. Nakazaki, K. Yamamoto, *J. Org. Chem.* **1976**, *41*, 1877.
[5] P. G. Gassman, T. J. van Bergen, D. P. Gilbert, B. W. Cue, *J. Am. Chem. Soc.* **1974**, *96*, 5495.
[6] D. H. Lloyd, D. E. Nichols, *Tetrahedron Lett.* **1983**, *24*, 4561; W. Haefliger, H. Knecht, *Tetrahedron Lett.* **1984**, *25*, 285.
[7] W. J. Houlihan, V. A. Parrino, Y. Uike, *J. Org. Chem.* **1981**, *46*, 4511.
[8] M. K. G. Mekhael, R. J. Smith, S. Bienz, A. Linden, H. Heimgartner, *Z. Naturforsch., B* **2002**, *57*, 444.
[9] M. K. G. Mekhael, H. Heimgartner, *Helv. Chim. Acta* **2003**, *86*, 2805.
[10] M. Rens, L. Ghosez, *Tetrahedron Lett.* **1970**, 3765; *cf.* L. Ghosez, J. Marchand-Brynaert, in 'Iminium Salts in Organic Chemistry', Eds. H. Böhme, H. G. Viehe, John Wiley & Sons, New York, 1976, p. 421; L. Ghosez, in 'Medicinal Chemistry V', Ed. J. Mathieu, Elsevier, Amsterdam, 1977, p. 363.
[11] H. Heimgartner, *Angew. Chem., Int. Ed.* **1991**, *30*, 238.
[12] B. P. Chandrasekhar, U. Schmid, R. Schmid, H. Heimgartner, H. Schmid, *Helv. Chim. Acta* **1975**, *58*, 1191.
[13] C. Bernard-Henriet, P. Hoet, L. Ghosez, R. Touillaux, *Tetrahedron Lett.* **1981**, *22*, 4717.
[14] P. Vittorelli, H. Heimgartner, H. Schmid, P. Hoet, L. Ghosez, *Tetrahedron* **1974**, *30*, 3737.
[15] P. Wipf, H. Heimgartner, *Helv. Chim. Acta* **1990**, *73*, 13.
[16] R. Luykx, C. B. Bucher, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 527.
[17] K. N. Koch, A. Linden, H. Heimgartner, *Tetrahedron* **2001**, *57*, 2311.
[18] T. R. Mihova, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 2067.
[19] B. Hostettler, J.-P. Obrecht, R. Prewo, J. H. Bieri, H. Heimgartner, *Helv. Chim. Acta* **1986**, *69*, 298.
[20] A. Rahm, A. Linden, B. R. Vincent, H. Heimgartner, M. Mühlstädt, B. Schulze, *Helv. Chim. Acta* **1991**, *74*, 1002.
[21] A. S. Orahovats, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1992**, *75*, 2515.

---

[3]) CCDC-212985 – 212987 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/products/csd/request, or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

[22] A. S. Orahovats, S. S. Bratovanov, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 1121.
[23] T. R. Mihova, A. Linden, H. Heimgartner, *Heterocycles* **1998**, *49*, 215.
[24] M. Schläpfer-Dähler, H. Heimgartner, *Helv. Chim. Acta* **1993**, *76*, 2398.
[25] F. Arnhold, S. Chaloupka, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 899.
[26] P. Hoet, 'Etude de la Réactivité des Amino-2 Azirines-1', Ph.D. thesis, Université Catholique de Louvain, 1975.
[27] M. Hugener, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1490.
[28] M. Hugener, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1823.
[29] A. D. Hughes, D. A. Price, O. Shishkin, N. S. Simpkins, *Tetrahedron Lett.* **1996**, *37*, 7607.
[30] J. M. Villalgordo, H. Heimgartner, *Helv. Chim. Acta* **1993**, *76*, 2830.
[31] P. Wipf, C. Jenny, H. Heimgartner, *Helv. Chim. Acta* **1987**, *70*, 1001.
[32] R. Luykx, C. B. Bucher, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 527.
[33] R. A. Breitenmoser, H. Heimgartner, *Helv. Chim. Acta* **2002**, *85*, 885.
[34] C. Jenny, H. Heimgartner, *Helv. Chim. Acta* **1986**, *69*, 374.
[35] C. B. Bucher, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 935.
[36] C. Strässler, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1997**, *80*, 1528.
[37] K. A. Brun, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2002**, *85*, 3422.
[38] S. Stamm, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2003**, *86*, 1371.
[39] M. K. G. Mekhael, Ph.D. thesis, Universität Zürich, 2003.
[40] J. Bernstein, R. E. Davies, L. Shimoni, N.-L. Chang, *Angew. Chem., Int. Ed.* **1995**, *34*, 1555.
[41] C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[42] R. R. Goehring, Y. P. Sachdeva, J. S. Pisipati, M. C. Sleevi, J. F. Wolfe, *J. Am. Chem. Soc.* **1985**, *107*, 435.
[43] C.-C. Yang, H.-T. Chang, J.-M. Fang, *J. Org. Chem.* **1993**, *58*, 3100.
[44] K. H. Shaughnessy, B. C. Hamann, J. F. Hartwig, *J. Org. Chem.* **1998**, *63*, 6546.
[45] L. A. Es'kova, E. V. Petrova, V. K. Turchaninov, M. F. Larin, G. G. Skvortsova, *Khim. Geterotsikl. Soedin.* **1989**, *7*, 924.
[46] R. Hooft, *KappaCCD Collect Software*, Nonius BV, Delft, The Netherlands, 1999.
[47] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, 'Macromolecular Crystallography', Part A, Eds. C. W. Carter Jr., R. M. Sweet, Academic Press, New York, 1997, p. 307.
[48] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[49] G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Germany (1997).
[50] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, p. 200.
[51] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[52] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[53] teXsan: Single Crystal Structure Analysis Software, Version 1.10, Molecular Structure Corporation, the Woodlands, Texas, 1999.

Received March 18, 2004