New Routes to Fused Isoquinolines

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Treatment of 6,7-diethoxy-3,4-dihydroisoquinoline (**8**) and its 1-methyl derivative **12** with hydrazonoyl halides **10** in the presence of Et_3N in THF under reflux afforded the corresponding 5,6-dihydro-1,2,4-triazolo[3,4-*a*]isoquinolines **11** and **13**, respectively, in high yield (*Schemes 2* and *3*). The products are formed *via* regioselective 1,3-dipolar cycloaddition of the intermediate nitrilimines **9** with the isoquinoline C=N bond. Reaction of 6,7-diethoxy-3,4-dihydroisoquinoline-1-acetonitrile (**4a**) with ethyl α-cyanocinnamates **15** in the presence of piperidine in refluxing MeCN yielded benzo[*a*]quinolizin-4-ones **16** (*Scheme 4*). Under the same conditions, **12** and arylidene malononitriles **19** reacted to give benzo[*a*]quinolizin-4-imines **20** (*Scheme 5*). Instead of **15** and **19**, mixtures of an aromatic aldehyde, and ethyl cyanoacetate or malononitrile, respectively, can be used in a one-pot reaction.

Introduction. – Within the class of fused isoquinolines with their cardiovascular [1], anti-inflammatory [2], and antidepressant [3] activities, [1,2,4]triazolo[3,4-*a*]isoquinolines are of considerable pharmaceutical and agricultural interest [4–7]. Therefore, the synthesis of this ring system is an attractive goal. A convenient approach is the 1,3-dipolar cycloaddition of nitrilimines [8–10], generated by elimination of HX from corresponding hydrazonoyl halides [11–13], to the C=N bond of 3,4-dihydroisoquinolines [12][14]. It has been shown that derivatives of type **1** can be obtained in high yields with $R^1 = H$ or alkyl [5][6][15][16]. On the other hand, 3,4-dihydroisoquinolin-1-acetonitriles and hydrazonoyl halides in refluxing THF in the presence of Et_3N reacted to give pyrrolo[2,1-*a*]isoquinoline derivatives of type **2** *via* a cyclocondensation reaction [15][17]. Spirocyclic adducts of type **3**, which could have been formed by 1,3-dipolar cycloaddition with the enamine tautomer of 3,4-dihydroisoquinolin-1-acetamide, have never been observed [6][15][17][3]).

The recently reported results of the reaction of hydrazonoyl halides with 3,4-dihydroisoquinolin-1-acetamide **4** in the presence of Et_3N [17] are in pronounced contrast to those published earlier [6]. Whereas the reaction of **5** in refluxing THF yielded only the cyclocondensation product **6**, the structure of the product obtained from the reaction in CH_2Cl_2 at room temperature was described as the cycloadduct **1a**

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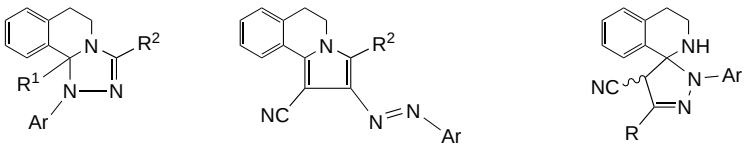
[2]) Swiss Federal Scholar ('*Bundesstipendiatin*') at the University of Zürich, October 1998–June 2000.

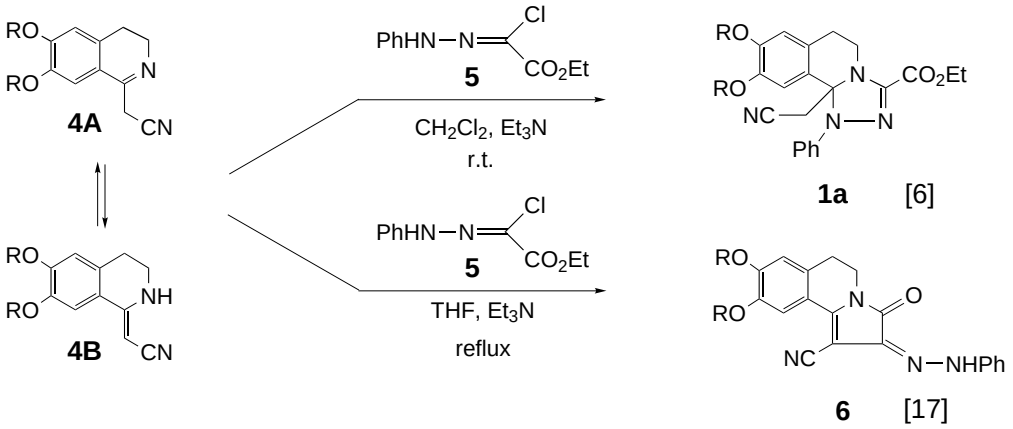
[3]) For a similar system in which cycloadditions with both the imine and the enamine tautomer occurred, see [18].



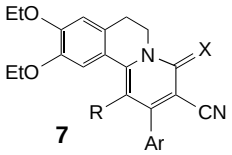
1 **2** **3**

(*Scheme 1*). In none of the reactions was the formation of a fused six-membered ring observed (*cf.* [6][15]).

Scheme 1



Isoquinoline derivatives with a fused six-membered ring at the C(1)–N(2) bond have also been studied extensively (*cf.* [19–21]). Among them, benzo[*a*]quinolizines are well-known, and several methods for their preparation have been reported [22–27]. In the present paper, we introduce a new and general route to polyfunctional benzo[*a*]quinolizine derivatives of type **7**, which compares favorably to the reported methods. The aim of this study is, on the one hand, to elaborate an efficient one-pot synthesis starting from inexpensive reactants and leading to **7** in good yields, and, on the other hand, to prepare compounds that might have pharmacological activity.



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Results and Discussion. – *1,3-Dipolar Cycloadditions with Nitrilimines.* Treatment of 6,7-diethoxy-3,4-dihydroisoquinoline (**8**) with nitrilimines **9a**–**h**, generated *in situ* by the action of Et_3N on the corresponding hydrazonoyl halides **10** in refluxing THF for 6 h, afforded, in each case, a single product as evidenced by means of TLC and ^{1}H-NMR analysis of the crude mixture. All products gave correct elemental analyses

and mass spectra for cycloadducts of type **11** (*Scheme 2* and *Table 1*), and IR and ^{1}H-NMR spectra supported the proposed structures. For example, a *singlet* at *ca.* 6.6 ppm in the ^{1}H-NMR spectrum ($CDCl_3$) was characteristic for H–C(10b).

Scheme 2

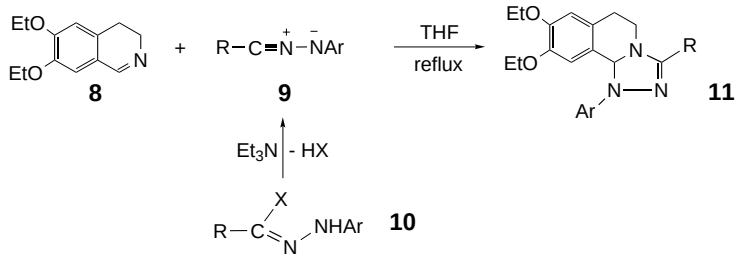


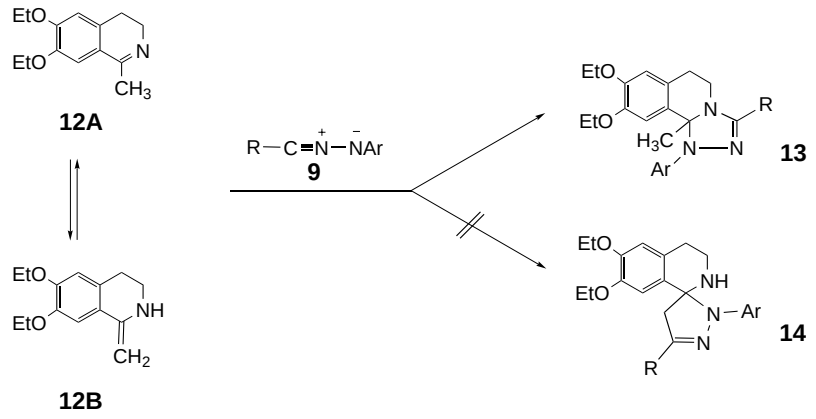
Table 1. *Reaction of 3,4-Dihydroisoquinoline* **8** *with Nitrilimines* **9a–h**

9	R	Ar	**11**	Yield [%]
a	PhCO	Ph	**a**	77
b	PhCO	4-MeC_6H_4	**b**	85
c	MeCO	Ph	**c**	81
d	MeCO	4-MeC_6H_4	**d**	78
e	(Thiophen-2-yl)carbonyl	Ph	**e**	82
f	MeOCO	Ph	**f**	78
g	MeOCO	4-MeC_6H_4	**g**	75
h	EtOCO	4-MeClC_6H_4	**h**	80

The second dipolarophile that was selected for our studies was 6,7-diethoxy-3,4-dihydro-1-methylisoquinoline (**12**), containing an 'active Me group' at C(1). The ability of **12** to behave either as a cyclic ketimine **12A** or as an enamine **12B** was discussed earlier (*e.g.*, [28][29]). Therefore, the main interest of the present study was whether the addition of nitrilimines **9** occurs at the C=N bond of **12A** or the C=C bond of **12B** (*Scheme 3*).

When the reactions of **12** with hydrazonoyl halides of type **10** were carried out under the same conditions as those involving **8** (Et_3N, THF, reflux), a single product was formed in each case, which was a cycloadduct of the corresponding nitrilimine (elemental analysis, MS). Structure **14** was eliminated on the basis of ^{1}H-NMR evidence: **14** was expected to reveal a *singlet* for CH_2 and an NH signal, but both were absent in the spectrum. Instead, the ^{1}H-NMR spectra ($CDCl_3$) of the products showed a *singlet* for an Me group at *ca.* 1.9 ppm, which is compatible with structure **13**. Indeed, the Me absorption of –N=C(Me)– in the starting material **12** appeared at 2.3 ppm. The shift of the signal by *ca.* 0.4 ppm towards higher field indicated the conversion of this group into the saturated moiety $-\overset{|}{N}-\overset{|}{C}(Me)-$ due to the cycloaddition at the C=N bond. Furthermore, the molecular structure of **13e** has been established by X-ray crystallography (*Fig.*).

Scheme 3



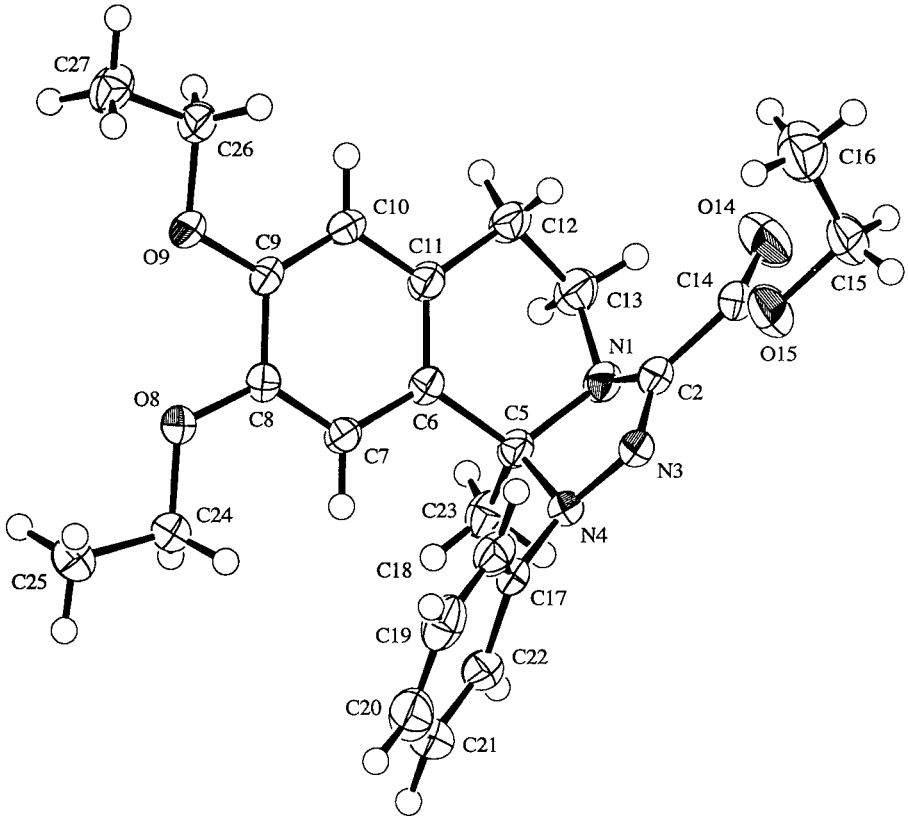


Figure. *ORTEP Plot* [30] *of the molecular structure of* **13e** (arbitrary numbering of the atoms; 50% probability ellisoids)

Table 2. *Reaction of 1-Methyl-3,4-dihydroisoquinoline* **12** *with Nitrilimines* **9**

9	R	Ar	**13**	Yield [%]
a	PhCO	Ph	**a**	81
b	PhCO	4-MeC_6H_4	**b**	83
c	MeCO	Ph	**c**	80
f	MeOCO	Ph	**d**	81
i	EtOCO	Ph	**e**	85
k	PhNHCO	Ph	**f**	86
l	PhNHCO	4-MeC_6H_4	**g**	85
m	Ph	Ph	**h**	80
n	PhCH=CH	Ph	**i**	78
o	Thiophen-2-yl	4-$NO_2C_6H_4$	**k**	80

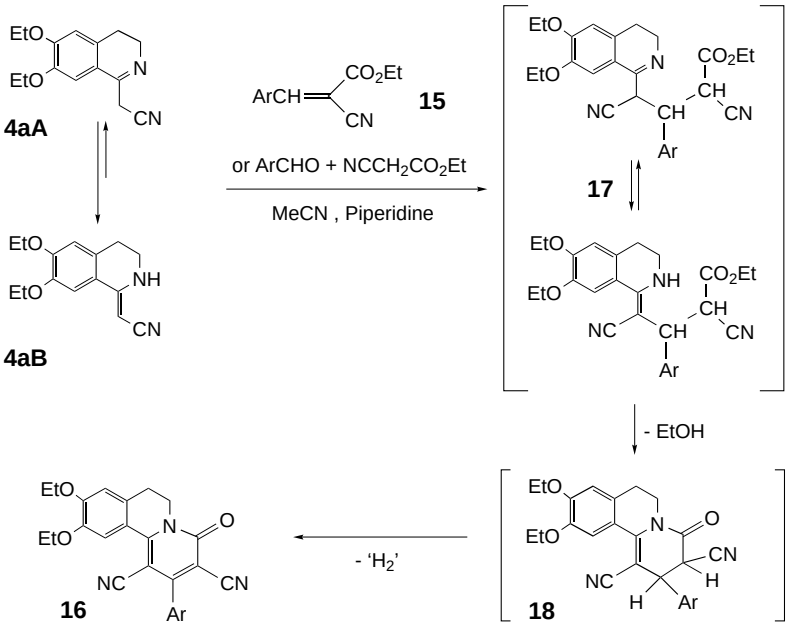
In conclusion, under the reaction conditions chosen the 1,3-dipolar cycloaddition of nitrilimines **9** with 3,4-dihydroisoquinoline **8** as well as with the 1-Me derivative **12** occurs exclusively at the C=N bond (*cf.* also [5][6][15]). This is in contrast to the recently reported reactions of hydrazonoyl halides with a 3,4-dihydroisoquinolin-1-acetonitrile derivative [17] in which no 1,3-dipolar cycloaddition took place, but pyrrolo[2,1-*a*]isoquinolines of type **2** were formed.

*Synthesis of Benzo[*a*]quinolizine Derivatives.* The reaction of 6,7-diethoxy-3,4-dihydroisoquinoline-1-acetonitrile (**4a**) with α-cyanocinnamates **15** in refluxing MeCN in the presence of piperidine afforded a single product **16** in each case, as evidenced by TLC (*Scheme 4*). The structures of the benzo[*a*]quinolizine derivatives **16** were established on the basis of their spectroscopic data (MS, ^{1}H-NMR, IR) and their elemental analyses. For example, the ^{1}H-NMR spectra ($CDCl_3$) revealed the absence of the ester EtO group, while the IR spectra (KBr) exhibited three bands near 2221 (C≡N), 2197 (C≡N), and 1666 cm^{-1} (CO lactam). In the case of **16a**, the ^{13}C-NMR spectrum of **16a** ((D_6)DMSO) supported the structure: characteristic signals appeared at 160.3 ppm for a lactam C=O, at 117.33 and 117.30 ppm for two C≡N groups, and at 99.7 and 88.9 for two sp^2-C-atoms bearing the CN groups. The same products **16** were also obtained in a one-pot reaction from equimolar amounts of **4a**, ethyl cyanoacetate, and arylaldehyde in refluxing MeCN in the presence of piperidine.

A conceivable reaction mechanism for the formation of **17** is proposed in *Scheme 4: Michael* addition of the enamine structure **4aB** (*cf.* [17]) with the cinnamates **15** yields the adducts **17**, which undergo a cyclization by elimination of EtOH, leading to **18**. The latter is then dehydrogenated by 'aromatization' to yield **16**.

In contrast to **4a**, there is no spectroscopic evidence for the presence of an enamine structure in the case of 3,4-dihydro-1-methylisoquinoline **12**, although some reactions have to be explained *via* the enamine tautomer (*cf.* [28][29]). Therefore, it was of interest to compare the reactivity of **12** with that of **4a**. Treatment of **12** with an equimolar amount of arylidenemalononitrile **19** in MeCN and piperidine under reflux yielded a single product in each case. For example, the reaction with benzylidenemalononitrile (**19**, Ar = Ph) gave a product with the molecular formula $C_{24}H_{23}N_3O_2$ (elemental analysis, MS). The same compound was formed in a one-pot reaction from **12**, malononitrile, and benzaldehyde under the same conditions. The IR spectrum (KBr) showed characteristic absorption bands at 3313 and 2202 cm^{-1} for NH and C≡N,

Scheme 4



a Ar = Ph; **b** Ar = 4-MeC_6H_4; **c** Ar = 4-MeOC_6H_4; **d** Ar =4-ClC_6H_4; **e** Ar = Thiophen-2-yl

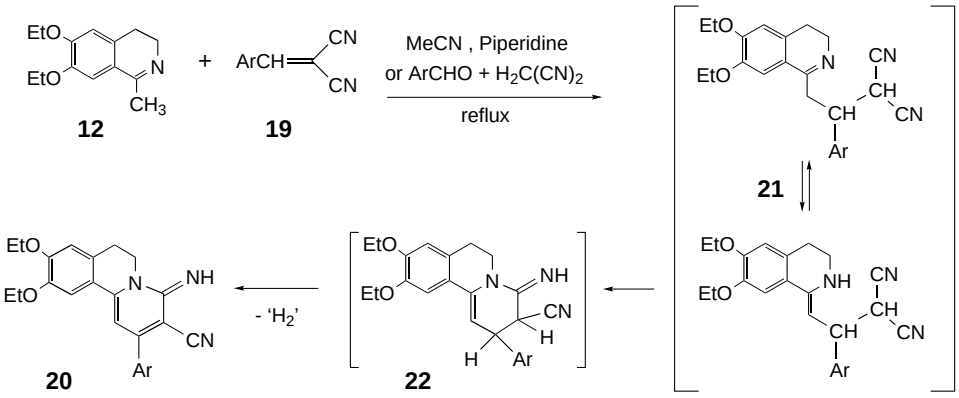
respectively, in accordance with the structure of the imino benzo[*a*]quinolizine derivative **20a** (*Scheme 5*). The MS exhibited a molecular ion peak at *m*/*z* 385 with high intensity, and the ^{1}H-NMR spectrum ($CDCl_3$) showed a characteristic *singlet* at 6.3 ppm assigned to H–C(1) of **20a**. Analogously, compounds **20b**–**h** were prepared from **12** and the corresponding benzylidenemalononitriles **19b**–**h**. The structures of these products were established on the basis of their spectroscopic data. The ^{13}C-NMR spectrum ((D$_6$)DMSO) of **20d** showed signals at 148.0 and 120.4 ppm, which could be assigned to the amidine C-atom (C(4)) and C(1), respectively. The characteristic absorptions are at 118.2 (C≡N) and 100.3 ppm (C(3)). Furthermore, propylidenemalononitrile (**19i**) and **12** reacted to give the benzo[*a*]quinolizine **20i** with an Et group at C(2) instead of Ar.

The formation of **20** is proposed to proceed analogously to that of **16**: *Michael* addition of the enamine tautomer of **12** with **19** gives the adduct **21**, which undergoes cyclization to yield **22**. Again, the latter is dehydrogenated spontaneously under the reaction conditions to give the final product **20**.

In summary, the reaction of 1-substituted 3,4-dihydroisoquinolines, which are able to undergo an imine/enamine tautomerism, with α-cyanocinnamates and benzylidenemalononitriles, respectively, opens a new and convenient route to benzo[*a*]quinazoline derivatives.

We thank the analytical units of our institutes for spectra and analyses. *E. M. A.* thanks the *Swiss Federal Government* for the provision of a *National Scholarship for Foreign Students.*

Scheme 5



a Ar = Ph; **b** Ar = 4-MeC_6H_4; **c** Ar = 4-$MeOC_6H_4$; **d** Ar = 4-ClC_6H_4; **e** Ar = 4-BrC_6H_4;
f Ar = Thiophen-2-yl; **g** Ar = 3,4-$(MeO)_2C_6H_3$; **h** Ar = 3,4-$(OCH_2O)C_6H_3$; **i** Ar = C_2H_5

Experimental Part

1. *General*. See [17]. Hydrazonoyl halides (chlorides or bromides) **10a**,**b** [31], **10c**,**d** [32], **10e** [33], **10f**,**g** [34], **10h** [35], **10i** [36], **10k**,**l** [37], **10m** [38], **10n** [39], and **10o** [40], and 3,4-dihydroisoquinolines **8** [17] and **12** [41], α-cyanocinnamates **15a**–**d** [42] and **15e** [43], and benzylidenemalononitriles **19a**–**d** [42], **19f** [44], **19h** [45], and **19i** [46] were prepared according to the procedures reported.

2. *Synthesis of 1,5,6,10b-Tetrahydro-1,2,4-triazolo[3,4-*a*]isoquinoline Derivatives* **11a**–**h**. To a soln. of a hydrazonoyl halide **10** (5 mmol) and 6,7-diethoxy-3,4-dihydroisoquinoline (**8**; 1.1 g, 5 mmol) in THF (40 ml) was added Et_3N (1.4 ml, 10 mmol) at r.t., and the mixture was refluxed for 6 h. The solvent was evaporated *i.v.*, and the residue was triturated with MeOH (10 ml) leading to solidification. The crude product was crystallized from EtOH or MeOH. The compounds **11a**–**h** with their physical data are listed below.

*3-Benzoyl-8,9-diethoxy-1,5,6,10b-tetrahydro-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline* (**11a**): 1.700 g (77%). M.p. 114° (EtOH). IR: 1643 (CO). EI-MS: 442 (13, $[M+1]^+$), 441 (49, $M^{+\cdot}$), 440 (100), 105 (15), 77 (6). Anal. calc. for $C_{27}H_{27}N_3O_3$ (441.54): C 73.45, H 6.16, N 9.52; found: C 73.30, H 6.02, N 9.24.

*3-Benzoyl-8,9-diethoxy-1,5,6,10b-tetrahydro-1-(4-methylphenyl)-1,2,4-triazolo[3,4-*a*]isoquinoline* (**11b**): 1.936 g (85%). M.p. 116° (EtOH). IR: 1635 (CO). ^{1}H-NMR: 1.29, 1.45 (2*t*, $J=7$, 2 *Me*CH_2); 2.30 (*s*, Me); 2.85 (*m*, CH_2); 3.88 (*m*, CH_2N); 4.10 (*m*, 2 CH_2O); 6.54 (*s*, H–C(10b)); 6.68, 6.75 (2*s*, 2 arom. H); 7.10–7.60 (*m*, 9 arom. H). EI-MS: 456 (14, $[M+1]^+$), 455 (69, $M^{+\cdot}$), 454 (100), 440 (8), 349 (6), 105 (15). Anal. calc. for $C_{28}H_{29}N_3O_3$ (455.57): C 73.83, H 6.41, N 9.22; found; C 73.54, H 6.14, N 9.02.

*3-Acetyl-8,9-diethoxy-1,5,6,10b-tetrahydro-1-phenyl-1,2,3-triazolo[3,4-*a*]isoquinoline* (**11c**): 1.537 g (81%). M.p. 107° (EtOH). IR: 1672 (CO). ^{1}H-NMR: 1.28, 1.45 (2*t*, $J=7$, 2 *Me*CH_2); 2.45 (*s*, Me); 2.71, 2.85 (2*m*, CH_2); 3.79 (*q*, $J=7$, CH_2O); 3.95 (*m*, CH_2N); 4.08 (*q*, $J=7$, CH_2O); 6.54 (*s*, H–C(10b)); 6.68, 6.72 (2*s*, 2 arom. H); 6.96 (*m*, 1 arom. H); 7.21 (*m*, 2 arom. H); 7.31 (*m*, 2 arom. H). EI-MS: 380 (11, $[M+1]^+$), 379 (60, $M^{+\cdot}$), 378 (100), 350 (5), 334 (5). Anal. calc. for $C_{22}H_{25}N_3O_3$ (379.46): C 69.64, H 6.63, N 11.07; found: C 69.92, H 6.44, N 11.19.

*3-Acetyl-8,9-diethoxy-1,5,6,10b-tetrahydro-1-(4-methylphenyl)-1,2,4-triazolo[3,4-*a*]isoquinoline* (**11d**): 1.535 g (78%). M.p. 111° (EtOH). IR: 1680 (CO). ^{1}H-NMR: 1.32, 1.51 (2*t*, $J=7$, 2 $MeCH_2$); 2.33, 2.44 (2*s*, 2 Me); 2.91 (*m*, CH_2); 3.80 (*m*, CH_2N); 4.12 (*m*, 2 CH_2O); 6.40 (*s*, H–C(10b)); 6.74, 6.84 (2*s*, 2 arom. H); 7.12–7.62 (*m*, 4 arom. H). Anal. calc. for $C_{23}H_{27}N_3O_3$ (393.49): C 70.21, H 6.91, N 10.68; found: C 70.50, H 6.58, N 10.41.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-1-phenyl-3-[(thiophen-2-yl)carbonyl]-1,2,4-triazolo[3,4-*a*]isoquinoline* (**11e**): 1.835 g (82%). M.p. 248° (EtOH). IR: 1681 (CO). EI-MS: 448 (15, $[M+1]^+$), 447 (61, $M^{+\cdot}$), 446 (100), 111 (14). Anal. calc. for $C_{25}H_{25}N_3O_3S$ (447.57): C 67.09, H 5.63, N 9.39, S 7.16; found: C 67.36, H 5.88, N 9.47, S 7.02.

*Methyl 8,9-Diethoxy-1,5,6,10b-tetrahydro-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxylate* (**11f**): 1.542 g (78%). M.p. 116° (EtOH). IR: 1722 (CO). ^{1}H-NMR: 1.20, 1.36 (2*t*, *J* = 7, 2 MeCH$_2$); 2.75 (*m*, CH$_2$); 3.62 (*m*, CH$_2$N); 3.73 (*q*, *J* = 7, CH$_2$O); 3.80 (*s*, MeO); 3.99 (*q*, *J* = 7, CH$_2$O); 6.37 (*s*, H–C(10b)); 6.61, 6.62 (2*s*, 2 arom. H); 6.82–7.27 (*m*, 5 arom. H). Anal. calc. for $C_{22}H_{25}N_3O_4$ (395.46): C 66.82, H 6.37, N 10.63; found: C 66.54, H 6.08, N 10.42.

*Methyl 8,9-Diethoxy-1,5,6,10b-tetrahydro-1-(4-methylphenyl)-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxylate* (**11g**): 1.536 g (75%). M.p. 132° (EtOH). IR: 1716 (CO). EI-MS: 410 (8, $[M+1]^+$), 409 (39, $M^{+\cdot}$), 408 (100), 350 (7), 349 (19), 295 (6), 105 (6), 91 (5). Anal. calc. for $C_{23}H_{27}N_3O_4$ (409.49): C 67.47, H 6.64, N 10.26; found: C 67.21, H 6.45, N 10.12.

*Ethyl 1-(4-Chlorophenyl)-8,9-diethoxy-1,5,6,10b-tetrahydro-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxylate* (**11h**): 1.776 g (80%). M.p. 141° (EtOH). IR: 1719 (CO). ^{1}H-NMR: 1.24, 1.27, 1.41 (3*t*, *J* = 7, 3 *Me*CH$_2$); 2.82 (*m*, CH$_2$); 3.72 (*m*, CH$_2$N); 3.85, 4.08, 4.35 (3*q*, *J* = 7, 3 CH$_2$O); 6.36 (*s*, H–C(10b)); 6.61, 6.70 (2*s*, 2 arom. H); 7.10 (*m*, 2 arom. H); 7.25 (*m*, 2 arom. H). Anal. calc. for $C_{23}H_{26}N_3O_4Cl$ (443.93): C 62.23, H 5.90, N 9.47; found: C 62.51, H 5.75, N 9.18.

3. *Synthesis of 1,5,6,10b-Tetrahydro-10b-methyl-1,2,4-triazolo[3,4-*a*]isoquinoline Derivatives* **13a**–**k**. These compounds were prepared according to the protocol in *Sect. 2* with 6,7-diethoxy-3,4-dihydro-1-methylisoquinoline **12** instead of **8**. The prepared compounds with their physical data are listed below.

*3-Benzoyl-8,9-diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13a**): 1.845 g (81%). M.p. 118° (MeOH). IR: 1665 (CO). EI-MS: 456 (6, $[M+1]^+$), 455 (8, $M^{+\cdot}$), 442 (6), 441 (45), 440 (100), 412 (5), 396 (13), 383 (7), 350 (5), 327 (7), 105 (37), 77 (17). Anal. calc. for $C_{28}H_{29}N_3O_3$ (455.56): C 73.83, H 6.41, N 9.22; found: C 73.71, H 6.54, N 9.27.

*3-Benzoyl-8,9-diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-(4-methylphenyl)-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13b**): 1.949 g (83%). M.p. 119° (EtOH). IR: 1665 (CO). ^{1}H-NMR: 1.19, 1.40 (2*t*, *J* = 7, 2 *Me*CH$_2$); 2.10, 2.30 (2*s*, 2 Me); 2.42, 2.92 (2*m*, CH$_2$); 3.32 (*q*, *J* = 7, CH$_2$O); 3.50 (*m*, 1 H of CH$_2$N); 4.02 (*q*, *J* = 7, CH$_2$O); 4.62 (*m*, 1 H of CH$_2$N); 5.95, 6.45 (2*s*, 2 arom. H); 7.05–8.10 (*m*, 9 arom. H). EI-MS: 470 (1, $[M+1]^+$), 469 (1, $M^{+\cdot}$), 456 (30), 455 (100), 454 (86), 105 (37), 77 (26). Anal. calc. for $C_{29}H_{31}N_3O_3$ (469.59): C 74.18, H 6.65, N 8.95; found: C 74.51, H 6.93, N 8.84.

*3-Acetyl-8,9-diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13c**): 1.574 g (80%). M.p. 104° (MeOH). IR: 1676 (CO). ^{1}H-NMR: 1.18, 1.40 (2*t*, *J* = 7, 2 *Me*CH$_2$); 2.09 (*s*, Me); 2.35, 2.88 (2*m*, CH$_2$); 2.44 (*s*, Me); 3.26 (*q*, *J* = 7, CH$_2$O); 3.48 (*m*, 1 H of CH$_2$N); 3.99 (*q*, *J* = 7, CH$_2$O); 4.65 (*m*, 1 H of CH$_2$N); 5.97, 6.44 (2*s*, 2 arom. H); 7.10–7.36 (*m*, 5 arom. H). Anal. calc. for $C_{23}H_{27}N_3O_3$ (393.49): C 70.21, H 6.91, N 10.68; found: C 70.46, H 6.72, N 10.44.

*Methyl 8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxylate* (**13d**): 1.658 g (81%). M.p. 114° (MeOH). IR: 1713 (CO). ^{1}H-NMR: 1.18, 1.40 (2*t*, *J* = 7, 2 *Me*CH$_2$); 2.08 (*s*, Me); 2.44, 2.94 (2*m*, CH$_2$); 3.27 (*q*, *J* = 7, CH$_2$O); 3.45 (*m*, 1 H of CH$_2$N); 3.85 (*s*, MeO); 3.99 (*q*, *J* = 7, CH$_2$O); 4.51 (*m*, 1 H of CH$_2$N); 5.94, 6.45 (2*s*, 2 arom. H); 7.07–7.30 (*m*, 5 arom. H). EI-MS: 410 (2, $[M+1]^+$), 409 (1, $M^{+\cdot}$), 396 (28), 395 (100), 350 (15), 234 (19), 91 (10), 77 (14). Anal. calc. for $C_{23}H_{27}N_3O_4$ (409.49): C 67.47, H 6.64, N 10.26; found: C 67.25, H 6.42, N 10.01.

*Ethyl 8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxylate* (**13e**): 1.800 g (85%). M.p. 137° (MeOH). IR: 1708 (CO). ^{1}H-NMR: 1.19, 1.35, 1.45 (3*t*, *J* = 7, 3 *Me*CH$_2$); 2.07 (*s*, Me); 2.44, 2.99 (2*m*, CH$_2$); 3.29 (*q*, *J* = 7, CH$_2$O); 3.50 (*m*, 1 H of CH$_2$N); 4.01, 4.35 (2*q*, *J* = 7, 2 CH$_2$O); 4.54 (*m*, 1 H of CH$_2$N); 5.93, 6.45 (2*s*, 2 arom. H); 7.09–7.33 (*m*, 5 arom. H). Anal. calc. for $C_{24}H_{29}N_3O_4$ (423.51): C 68.07, H 6.89, N 9.92; found: C 68.24, H 6.72, N 9.65.

Recrystallization from MeOH gave suitable crystals for an X-ray-diffraction analysis.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1,*N*-diphenyl-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxamide* (**13f**): 2.023 g (86%). M.p. 113° (EtOH). IR: 3210 (NH), 1670 (CO). ^{1}H-NMR: 1.40, 1.52 (2*t*, *J* = 7, 2 *Me*CH$_2$); 1.83 (*s*, Me); 2.42, 2.73 (2*m*, CH$_2$); 3.02, 3.82 (2*m*, CH$_2$N); 3.91, 4.14 (2*q*, *J* = 7, 2 CH$_2$O); 6.63, 6.84 (2*s*, 2 arom. H); 7.10–7.82 (*m*, 10 arom. H); 9.13 (*s*, NH). EI-MS: 471 (6, $[M+1]^+$), 470 (3, $M^{+\cdot}$), 458 (6), 457 (35), 456 (100), 455 (99), 428 (6), 351 (5), 91 (11), 77 (15). Anal. calc. for $C_{28}H_{30}N_4O_3$ (470.58): C 71.47, H 6.42, N 11.91; found: C 71.33, H 6.25, N 11.84.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-(4-methylphenyl)-*N*-phenyl-1,2,4-triazolo[3,4-*a*]isoquinoline-3-carboxamide* (**13g**): 2.060 g (85%). M.p. 165° (EtOH). IR: 3255 (NH), 1681 (CO). ^{1}H-NMR: 1.42, 1.54 (2*t*, *J* = 7, 2 *Me*CH$_2$); 1.72, 2.33 (2*s*, 2 Me); 2.42, 2.64 (2*m*, CH$_2$); 3.14, 3.73 (2*m*, CH$_2$N); 3.82, 4.14 (2*q*, *J* = 7, 2 CH$_2$O); 6.53, 6.71 (2*s*, 2 arom. H); 7.00–7.72 (*m*, 9 arom. H); 9.11 (*s*, NH). Anal. calc. for $C_{29}H_{32}N_4O_3$ (484.61): C 71.88, H 6.65, N 11.56; found: C 71.62, H 6.82, N 11.34.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1,3-diphenyl-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13h**): 1.710 g (80%). M.p. 129° (MeOH). ^{1}H-NMR: 1.33, 1.43 (2*t*, *J* = 7, 2 *Me*CH_2); 1.80 (*s*, Me); 2.38, 2.80 (2*m*, CH_2); 3.13, 3.70 (2*m*, CH_2N); 3.82, 4.04 (2*q*, *J* = 7, 2 CH_2O); 6.55, 6.56 (2*s*, 2 arom. H); 6.96–7.78 (*m*, 10 arom. H). EI-MS: 429 (6), 428 (32, $[M+1]^+$), 427 (77, $M^{+\bullet}$), 414 (53), 413 (77), 412 (100), 368 (71), 355 (38), 326 (25), 310 (24), 204 (17), 194 (31), 185 (11), 176 (29), 104 (9), 92 (16), 77 (31). Anal. calc. for $C_{27}H_{29}N_3O_2$ (427.55): C 75.86, H 6.83, N 9.83; found: C 75.72, H 6.63, N 9.87.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-phenyl-3-(2-phenylethenyl)-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13i**): 1.769 g (78%). M.p. 103° (MeOH). ^{1}H-NMR: 1.28, 1.40 (2*t*, *J* = 7, 2 *Me*CH_2); 1.88 (*s*, Me); 2.48, 2.98 (2*m*, CH_2); 3.26 (*m*, 1 H of CH_2N); 3.65 (*q*, *J* = 7, CH_2O); 3.86 (*m*, 1 H of CH_2N); 4.06 (*q*, *J* = 7, CH_2O); 6.38, 6.55 (2*s*, 2 arom. H); 6.77 (*d*, *J* = 16, 1 H of PhCH=CH); 7.03 (*m*, 1 arom. H); 7.10–7.39 (*m*, 8 H); 7.51 (*m*, 2 arom. H). EI-MS: 454 (6, $[M+1]^+$), 453 (15, $M^{+\bullet}$), 440 (8), 439 (48), 438 (100), 394 (18), 381 (8), 212 (6), 91 (16). Anal. calc. for $C_{29}H_{31}N_3O_2$ (453.59): C 76.80, H 6.88, N 9.26; found: C 76.54, H 6.62, N 9.47.

*8,9-Diethoxy-1,5,6,10b-tetrahydro-10b-methyl-1-(4-nitrophenyl)-3-(thiophen-2-yl)-1,2,4-triazolo[3,4-*a*]isoquinoline* (**13k**): 1.914 g (80%). M.p. 162° (MeOH). ^{1}H-NMR: 1.25, 1.43 (2*t*, *J* = 7, 2 *Me*CH_2); 1.80 (*s*, Me); 2.33, 2.70 (2*m*, CH_2); 3.12, 3.80 (2*m*, CH_2N); 3.71, 4.01 (2*q*, *J* = 7, 2 CH_2O); 6.55, 6.70 (2*s*, 2 arom. H); 6.82–8.20 (*m*, 7 arom. H). Anal. calc. for $C_{25}H_{26}N_4O_4S$ (478.58): C 62.75, H 5.47, N 11.71, S 6.70; found: C 62.48, H 5.65, N 11.62, S 6.60.

4. *Synthesis of Benzo[*a*]quinolizinone Derivatives* **16a–e.** *Method A:* A mixture of equimolar amounts of the appropriate aryl aldehyde, ethyl cyanoacetate, and 6,7-diethoxy-3,4-dihydroisoquinolin-1-acetonitrile (**4a**) in MeCN (40 ml) and piperidine (4 drops) was heated under reflux for 6 h. The solvent was evaporated *i.v.*, and the residue was triturated with MeOH (10 ml), resulting in solidification. The crude product was crystallized from EtOH to give **16a–e**.

Method B: To a soln. of **4a** (1.29 g, 5 mmol) and ethyl α-cyanocinnamates **15a–e** (5 mmol) in MeCN (40 ml) was added piperidine (4 drops) at r.t. Similar treatment of the mixture as in *Method A* gave products that were identical in all respects (m.p., mixed m.p., IR, ^{1}H-NMR, MS) with those obtained by *Method A*. The products **16a–e** obtained and their physical data are listed below.

*9,10-Diethoxy-6,7-dihydro-4-oxo-2-phenylbenzo[*a*]quinolizine-1,3-dicarbonitrile* (**16a**): 1.543 g (75%). M.p. 224° (EtOH). IR: 2214, 2195 (CN), 1666 (CO). ^{1}H-NMR: 1.28, 1.45 (2*t*, *J* = 7, 2 *Me*CH_2); 2.88–3.05 (*m*, CH_2); 3.8 (*m*, CH_2N); 4.10 (*q*, *J* = 7, 2 CH_2O); 6.45–7.35 (*m*, 7 arom. H). ^{13}C-NMR ((D_6)DMSO): 14.4, 14.5 (2 *Me*CH_2); 26.1 (CH_2); 40.4 (CH_2N); 64.20, 64.24 (2 CH_2O); 88.9, 99.7 (C(1), C(3)); 111.7, 113.6, 115.0 (3 C); 117.30, 117.33 (2 CN); 128.2, 128.6, 130.5, 134.0, 134.1, 146.1, 152.9, 153.5, 158.2 (14 C); 160.3 (C(4)=O). EI-MS: 411 (100, $M^{+\bullet}$), 382 (42), 354 (89), 339 (17), 326 (26), 313 (34), 280 (20), 242 (8), 214 (11), 171 (13), 129 (11), 107 (13), 77 (5). Anal. calc. for $C_{25}H_{21}N_3O_3$ (411.46): C 72.98, H 5.14, N 10.21; found: C 72.75, H 5.02, N 10.06.

*9,10-Diethoxy-6,7-dihydro-(4-methylphenyl)-4-oxobenzo[*a*]quinolizine-1,3-dicarbonitrile* (**16b**): 1.638 g (77%): M.p. 220° (EtOH). IR: 2214, 2189 (CN), 1666 (CO). ^{1}H-NMR: 1.41–1.59 (*m*, 2 *Me*CH_2); 2.45 (*s*, Me); 2.95 (*t*-like, CH_2); 4.15–4.39 (*m*, CH_2N, 2 CH_2O); 6.80 (*s*, 1 arom. H); 7.32–7.50 (*m*, 4 arom. H); 7.93 (*s*, 1 arom. H). EI-MS: 425 (20, $M^{+\bullet}$), 368 (99), 313 (51), 218 (55), 160 (43), 137 (34), 129 (100), 123 (53), 109 (44), 103 (51), 97 (37), 83 (73). Anal. calc. for $C_{26}H_{23}N_3O_3$ (425.49): C 73.40, H 5.44, N 9.88; found: C 73.13, H 5.25, N 9.72.

*9,10-Diethoxy-6,7-dihydro-2-(4-methoxyphenyl)-4-oxobenzo[*a*]quinolizine-1,3-dicarbonitrile* (**16c**): 1.766 g (80%). M.p. 204° (EtOH). IR: 2214, 2197 (CN), 1658 (CO). ^{1}H-NMR: 1.40–1.59 (*m*, 2 *Me*CH_2); 2.95 (*t*-like, CH_2); 3.88 (*s*, MeO); 4.10–4.35 (*m*, CH_2N, 2 CH_2O); 6.80 (*s*, 1 arom. H); 7.05 (*d*-like, 2 arom. H); 7.55 (*d*-like, 2 arom. H); 7.93 (*s*, 1 arom. H). EI-MS: 441 (15, $M^{+\bullet}$), 383 (54), 368 (100), 341 (51), 284 (28), 262 (39), 242 (45), 239 (55), 193 (10), 187 (40), 146 (50), 125 (34), 112 (100), 102 (68). Anal. calc. for $C_{26}H_{23}N_3O_4$ (441.49): C 70.74, H 5.25, N 9.52; found: C 70.52, H 5.14, N 9.36.

*2-(4-Chlorophenyl)-9,10-diethoxy-6,7-dihydro-4-oxobenzo[*a*]quinolizine-1,3-dicarbonitrile* (**16d**): 1.739 g (78%). M.p. 220° (EtOH). IR: 2221, 2197 (CN), 1666 (CO). ^{1}H-NMR: 1.40–1.59 (*m*, 2 *Me*CH_2); 2.95 (*t*-like, CH_2); 4.09–4.36 (*m*, CH_2N, 2 CH_2O); 6.82 (*s*, 1 arom. H); 7.45–7.60 (*m*, 4 arom. H); 7.90 (*s*, 1 arom. H). EI-MS: 446 (31, $M^{+\bullet}$), 445 (100), 388 (49), 354, 296 (18), 268 (8), 250 (44), 242 (16), 214 (11), 191 (24), 169 (32), 128 (25), 108 (59), 77 (15). Anal. calc. for $C_{25}H_{20}N_3O_3Cl$ (445.91): C 67.34, H 4.52, N 9.42; found: C 67.16, H 4.41, N 9.22.

*9,10-Diethoxy-6,7-dihydro-4-oxo-2-(thiophen-2-yl)benzo[*a*]quinolizine-1,3-dicarbonitrile* (**16e**): 1.670 g (80%). M.p. 265° (EtOH). IR: 2210, 2197 (CN), 1662 (CO). ^{1}H-NMR: 1.41–1.59 (*m*, 2 *Me*CH_2); 2.95 (*t*-like, CH_2); 4.13–4.35 (*m*, CH_2N, 2 CH_2O); 6.80 (*s*, 1 arom. H); 7.21–7.73 (*m*, 3 arom. H); 7.92 (*s*, 1 arom. H). Anal. calc. for $C_{23}H_{19}N_3O_3S$ (417.49): C 66.17, H 4.58, N 10.07; found: C 66.11, H 4.53, N 10.01.

5. *Synthesis of Benzo[*a*]quinolizine Derivatives* **20a**–**i**. *Method A:* Equimolar amounts of **12**, the appropriate aldehyde, and malononitrile in MeCN, in the presence of piperidine, were heated under reflux for 3 h. The solvent was evaporated *i.v.*, and the residue was triturated with MeOH (10 ml), leading to solidification. The crude product was crystallized from EtOH or MeOH.

Method B: To a soln. of **12** (1.2 g, 5 mmol) and arylidinemalononitrile **19** (5 mmol) in MeCN (40 ml) was added piperidine (0.5 ml) at r.t., and the mixture was refluxed for 3 h. Workup as in *Method A* yielded products identical in all respects to those obtained from *Method A*. The compounds **20a**–**i** prepared together with their physical data are listed below.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-phenyl-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20a**): 1.735 g (90%). M.p. 176° (EtOH). IR: 3313 (NH), 2202 (CN). ^{1}H-NMR: 1.40–1.58 (*m*, 2 *Me*CH_2); 2.90–3.03 (*m*, CH_2); 4.03–4.25 (*m*, CH_2N, CH_2O); 4.27–4.39 (*m*, CH_2O); 6.30, 6.76, 6.88, 7.20 (4*s*, 3 arom. H, NH); 7.50–7.71 (*m*, 5 arom. H). EI-MS: 385 (100, $M^{+\cdot}$), 356 (70), 328 (27), 300 (16), 165 (9). Anal. calc. for $C_{24}H_{23}N_3O_2$ (385.50): C 74.78, H 6.01, N 10.90; found: C 74.54, H 5.82, N 10.73.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-(4-methylphenyl)-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20b**): 1.740 g (87%). M.p. 184° (EtOH). IR: 3312 (NH), 2197 (CN). ^{1}H-NMR: 1.40–1.56 (*m*, 2 *Me*CH_2); 2.40 (*s*, Me); 2.90–3.02 (*m*, CH_2); 4.03–4.23 (*m*, CH_2N, CH_2O); 4.27–4.38 (*m*, CH_2O); 6.23, 6.75, 6.88, 7.30 (4*s*, 3 arom. H, NH); 7.40 (*d*-like, 2 arom. H); 7.53 (*d*-like, 2 arom. H). Anal. calc. for $C_{25}H_{25}N_3O_2$ (399.53): C 75.17, H 6.30, N 10.52; found: C 75.36, H 6.54, N 10.41.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-(4-methoxyphenyl)-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20c**): 1.808 g (87%). M.p. 148° (EtOH). IR: 3320 (NH), 2200 (CN). ^{1}H-NMR: 1.41–1.56 (*m*, 2 *Me*CH_2); 2.90–3.02 (*m*, CH_2); 3.90 (*s*, MeO); 4.04–4.23 (*m*, CH_2N, CH_2O); 4.26–4.37 (*m*, CH_2O); 6.23, 6.75, 6.87 (3*s*, 2 arom. H, NH); 7.01 (*d*-like, 2 arom. H); 7.20 (*s*, 1 arom. H); 7.61 (*d*-like, 2 arom. H). EI-MS: 415 (100, $M^{+\cdot}$), 414 (95), 386 (89), 358 (21), 330 (16), 300 (5), 180 (14). Anal. calc. for $C_{25}H_{25}N_3O_3$ (415.53): C 72.27, H 6.06, N 10.11; found: C 72.54, H 6.17, N 10.02.

*2-(4-Chlorophenyl)-9,10-diethoxy-6,7-dihydro-4-imino-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20d**): 1.785 g (85%). M.p. 217° (EtOH). IR: 3312 (NH), 2203 (CN). ^{1}H-NMR: 1.41–1.57 (*m*, 2 *Me*CH_2); 2.91–3.02 (*m*, CH_2); 4.04–4.24 (*m*, CH_2N, CH_2O); 4.28–4.38 (*m*, CH_2O); 6.20, 6.75, 6.88, 7.30 (4*s*, 3 arom. H, NH); 7.44–7.62 (*m*, 4 arom. H). ^{13}C-NMR ((D_6)DMSO): 15.3 (2 *Me*CH_2); 27.1 (CH_2); 46.0 (CH_2N); 64.7, 65.1 (2 CH_2O); 100.3 (C(3)); 112.2, 112.4 (2 C); 118.2 (CN); 120.4, 129.4, 130.6, 130.9, 135.5, 136.3, 148.1, 152.3, 154.4 (14 C); 157.2 (C=NH). Anal. calc. for $C_{24}H_{22}N_3O_2Cl$ (419.91): C 68.65, H 5.28, N 10.01; found: C 68.91, H 5.54, N 9.92.

*2-(4-Bromophenyl)-9,10-diethoxy-6,7-dihydro-4-imino-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20e**): 1.857 g (80%). M.p. 225° (EtOH). IR: 3312 (NH), 2202 (CN). ^{1}H-NMR: 1.40–1.56 (*m*, 2 *Me*CH_2); 2.90–3.03 (*m*, CH_2); 4.04–4.24 (*m*, CH_2N, CH_2O); 4.28–4.39 (*m*, CH_2O); 6.20, 6.75, 6.80, 7.30 (4*s*, 3 arom. H, NH); 7.50 (*d*-like, 2 arom. H); 7.71 (*d*-like, 2 arom. H). EI-MS: 464 (25, $M^{+\cdot}$), 408 (6), 359 (32), 267 (8), 123 (18), 83 (20), 77 (14), 69 (19), 56 (100). Anal. calc. for $C_{24}H_{22}N_3O_2Br$ (464.37): C 62.08, H 4.77, N 9.05; found: C 62.25, H 4.72, N 9.00.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-(thiophen-2-yl)-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20f**): 1.605 g (82%). M.p. 190° (EtOH). IR: 3316 (NH), 2197 (CN). ^{1}H-NMR: 1.45–1.57 (*m*, 2 *Me*CH_2); 2.91–3.03 (*m*, CH_2); 4.08–4.23 (*m*, CH_2N, CH_2O); 4.27–4.36 (*m*, CH_2O); 6.35, 6.75, 6.86, 7.26 (4*s*, 3 arom. H, NH); 7.44, 7.61, 7.94 (3 br. *s*, 3 arom. H). Anal. calc. for $C_{22}H_{21}N_3O_2S$ (391.49): C 67.50, H 5.40, N 10.73, S 8.19; found: C 67.82, H 5.08, N 10.52, S 8.04.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-(3,4-dimethoxyphenyl)-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20g**): 1.916 g (86%). M.p. 185° (MeOH). IR: 3321 (NH), 2194 (CN). ^{1}H-NMR: 1.39–1.57 (*m*, 2 *Me*CH_2); 2.90–3.01 (*m*, CH_2); 3.94, 4.00 (2*s*, 2 MeO); 4.05–4.23 (*m*, CH_2N, CH_2O); 4.26–4.38 (*m*, CH_2O); 6.30, 6.75, 6.86, 7.10 (4*s*, 3 arom. H, NH); 7.24–7.34 (*m*, 3 arom. H). Anal. calc. for $C_{26}H_{27}N_3O_4$ (445.53): C 70.10, H 6.10, N 9.43; found: C 70.32, H 6.34, N 9.15.

*9,10-Diethoxy-6,7-dihydro-4-imino-2-[3,4-(methylenedioxy)phenyl]-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20h**): 1.890 g (88%). M.p. 172° (MeOH). IR: 3311 (NH), 2201 (CN). ^{1}H-NMR: 1.42–1.57 (*m*, 2 *Me*CH_2); 2.90–3.02 (*m*, CH_2); 4.04–4.22 (*m*, CH_2N, CH_2O); 4.28–4.38 (*m*, CH_2O); 6.10 (*s*, CH_2O_2); 6.21, 6.75, 6.83, 7.04 (4*s*, 3 arom. H, NH); 7.10–7.31 (*m*, 3 arom. H). EI-MS: 429 (14, $M^{+\cdot}$), 428 (14), 359 (38), 299 (19), 267 (11), 201 (14), 171 (16), 123 (16), 102 (43), 56 (100). Anal. calc. for $C_{25}H_{23}N_3O_4$ (429.49): C 69.92, H 5.39, N 9.78; found: C 69.64, H 5.56, N 9.62.

*9,10-Diethoxy-2-ethyl-6,7-dihydro-4-imino-4*H-*benzo[*a*]quinolizine-3-carbonitrile* (**20i**): 1.383 g (82%). M.p. 173° (EtOH). IR: 3319 (NH), 2198 (CN). ^{1}H-NMR: 1.30 (*t*, $J = 7$, *Me*CH_2); 1.42–1.57 (*m*, 2 *Me*CH_2); 2.64 (*q*, $J = 7$, Me*C*H_2); 2.85–2.96 (*m*, CH_2); 4.08–4.19 (*m*, CH_2N, CH_2O); 4.20–4.32 (*m*, CH_2O); 6.10, 6.74,

6.88, 7.30 (4*s*, 3 arom. H, NH). EI-MS: 337 (87, $M^{+\cdot}$), 336 (100), 309 (74), 308 (82), 280 (23), 252 (17), 237 (6). Anal. calc. for $C_{20}H_{23}N_3O_2$ (337.42): C 71.20, H 6.86, N 12.45; found: C 71.51, H 6.64, N 12.17.

6. *Crystal-Structure Determination of* **13e** (see *Table 3* and *Fig.*)[4]). All measurements were performed on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating-anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects but not for absorption. Data collection and refinement parameters are given in *Table 3*, and a view of the molecule is shown in the *Figure*. The structure was solved by direct methods using

Table 3. *Crystallographic Data of Compound* **13e**

Crystallized from	MeOH
Empirical formula	$C_{24}H_{29}N_3O_4$
Formula weight [g mol^{-1}]	423.51
Crystal color, habit	pale yellow, tablet
Crystal dimensions [mm]	$0.15 \times 0.43 \times 0.45$
Temp. [K]	173(1)
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
Reflections for cell determination	25
2θ Range for cell determination [°]	37 – 40
Unit-cell parameters a [Å]	12.198(2)
b [Å]	13.076(1)
c [Å]	7.308(2)
α [°]	98.78(2)
β [°]	106.13(2)
γ [°]	85.44(1)
V [Å^3]	1105.7(4)
D_x [g cm^{-3}]	1.272
μ(MoK_α) [mm^{-1}]	0.0873
$2\theta_{(max)}$ [°]	55
Total reflections measured	5317
Symmetry-independent reflections	5077
Reflections used [$I > 2\sigma(I)$]	3671
Parameters refined	281
Final R	0.0540
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0516
Goodness-of-fit	2.335
Secondary extinction coefficient	$1.5(2) \times 10^{-6}$
Final Δ_{max}/σ	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.50; -0.31

SHELXS86 [47], which revealed the position of all non-H atoms. The non-H atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom. Refinement of the structure was carried out on F according to full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was applied. Neutral-atom-scattering factors for non-H atoms were taken from [48a] and the scattering factors for H-atoms from [49]. Anomalous dispersion effects

[4]) Crystallographic data (excluding structure factors) for the structure **13e** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-145106. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-(0)1223-336 033 or e-mail: deposit@ccdc.cam.ac.uk).

were included in F_c [50]; the values for f' and f'' were those of [48b], and the values of the mass attenuation coefficients were those of [48c]. All calculations were performed with the *TEXSAN* crystallographic software package [51].

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