v-Triazolines. Part 40.[1] Thermal and photochemical transformations of 1-biaryl-5-amino-4,5-dihydro-*v*-triazoles: a new synthetic approach to 6-alkylphenanthridines and aza-analogs

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1-Biaryl-5-morpholino-*v*-triazolines **4** were prepared from aliphatic aldehydes **1**, morpholine and 2-azidobiaryls **3**. They underwent smooth thermal rearrangement to tertiary amidines **5** which were photochemically cyclized to 6-alkylphenanthridines **6a**,**b**,**e**,**f** and analogs **6c**,**d** and **8a**,**b** with morpholine elimination. Direct photolysis of triazolines **4** afforded lower yields of the same compounds **6** together with by-products indicative of the mechanism of the photochemical rearrangement which is discussed.

Introduction

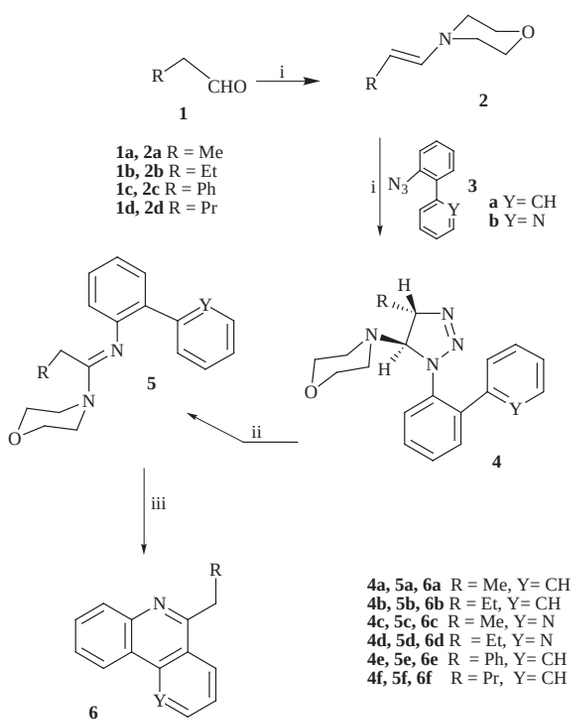
The thermal behavior of 4,5-dihydro-*v*-triazoles (*v*-triazolines) has been extensively studied[2] and previous and recent work of our research group has explored the use of the thermal transformations of several 5-amino-*v*-triazolines as a synthetic tool for the direct or indirect preparation of nitrogen-containing heterocycles *e.g.* quinoxalines,[3] functionalized quinolines,[4] oxopyridines,[5] benzimidazoles,[6] quinazolines.[7]

However, the photochemistry of 5-amino-*v*-triazolines has been considered only occasionally,[2,8] in contrast to that of alkyl- and aryl-substituted-*v*-triazolines without an amino substituent which has received ample attention and is now considered one of the methods of choice for aziridine generation.[2] The photochemical transformations of this particular class of *v*-triazolines, and their synthetic potential, have never been fully explored.

The present paper is concerned with our results on thermal and photochemical reactions of some 1-biaryl-5-morpholino-*v*-triazolines and related *N*-biarylamidines and with new synthetic approaches to 6-alkylphenanthridines and analogs.

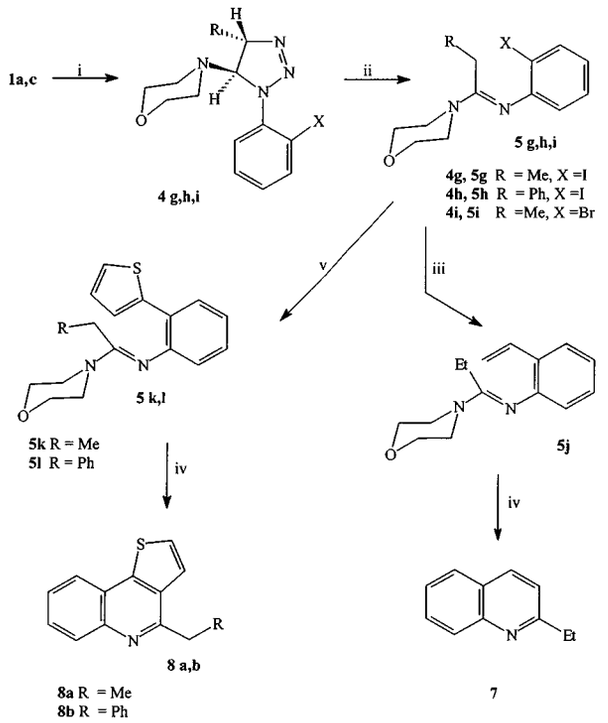
Results

Triazolines **4a**–**f** were readily obtained by the three-component reaction of 2-azidobiphenyl **3a** or 2-(2-azidophenyl)pyridine **3b** with aliphatic aldehydes **1a**–**d** and morpholine, through cycloaddition of the azide to the intermediate enamines **2a**–**d** which are produced in the equilibrium reaction with their parent compounds (Scheme 1). The structure and *trans* configuration of all products were confirmed by ^{1}H NMR data. Prolonged heating of compounds **4** in boiling xylene resulted in nitrogen extrusion and transposition of the H-atom linked to H-5 according to a well established mechanism.[2] The tertiary amidines **5a**–**f** were produced in satisfactory yield. Irradiation of compounds **5** in benzene solution and at room temperature with a high pressure Hg-lamp with Pyrex filter for a short time resulted in cyclization, elimination of the morpholine group and formation, in good yield, of the corresponding 6-alkylphenanthridines **6a**,**b**,**e**,**f** and 5-alkylbenzo[*h*][1,6]naphthyridines **6c**,**d**, respectively. No significant by-products were formed in the thermal transformation of compounds **4** nor in the photocyclization step of intermediates **5**. The structure of the phenanthridines and naphthyridines was unequivocally established by NMR data and, in the case of known compounds, by comparison with reported physical data.



Scheme 1 *Reagents and conditions*: i, toluene, morpholine, room temp., 12–48 h, Na_2SO_4; ii, *p*-xylene, reflux, 3–5 h; iii, PhH, *hv*.

As an extension of this synthetic scheme the vinylation and arylation of *N*-(2-haloaryl)amidines was considered (Scheme 2). The bromo- and iodoamidines **5g**–**i** were prepared by thermal rearrangement of the corresponding triazolines **4g**–**i** obtained as above from the corresponding aldehydes and 2-bromo- and 2-iodophenyl azide, respectively. By reaction of **5i** with tributyl(vinyl)stannane in the presence of tetrakis(triphenylphosphine)palladium and of **5g**,**h** with tributyl(2-thienyl)stannane in presence of bis(triphenylphosphine)palladium dichloride the amidines **5j** and **5k**,**l** were easily obtained. Following irradiation of these amidines 2-ethylquinoline **7** and the thieno[3,2-*c*]quinolines **8a**,**b** were prepared.



Scheme 2 *Reagents and conditions:* i, PhH, morpholine, room temp., 2-bromophenyl azide or 2-iodophenyl azide; ii, *p*-xylene, reflux; iii, $Bu_3SnCH{=}CH_2$, $(PPh_3)_4Pd$, toluene, reflux; iv, *hv*; v, tributyl(2-thienyl)-stannane, $Pd(PPh_3)_2Cl_2$.

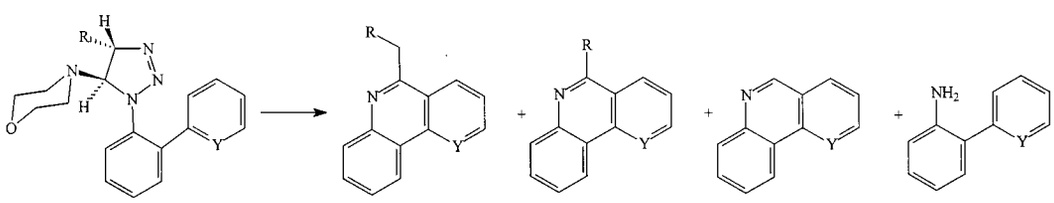
A far more complicated reaction pattern was offered by the direct irradiation of triazolines **4**, in benzene solution, with a high-pressure Hg-lamp with Pyrex filter. The photochemical transformation required a reaction time of about 15–20 hours until completion and several products were formed under these conditions. In Scheme 3 the products of each reaction are listed, together with their yields, determined by isolation or HPLC analysis in comparison with authentic samples.

Triazoline **4a** afforded a reaction mixture from which 6-ethylphenanthridine **6a** was isolated as the major substance. Besides, traces of 6-methylphenanthridine **6g** (containing a carbon atom less in the alkyl group), phenanthridine **6h** and 2-aminobiphenyl **9a** were obtained by chromatographic separation. Similar results were obtained by irradiation of **4c** and **4d**. In all cases the expected benzo[*h*][1,6]naphthyridines (**6c** and **6d**, respectively) were formed as the main products. Smaller amounts of the compounds containing a carbon atom less in the alkyl substituent (5-methylbenzo[*h*][1,6]naphthyridine **6i** and **6c** respectively), benzo[*h*][1,6]naphthyridine **6j** and 2-(2-pyridyl)aniline **9b** were also found. From **4e** only the phenanthridine **6e** (main product) and **6h** and **9a** could be isolated. The longer-chain triazoline **4f** behaved similarly, affording **9a** and **6f** as the main products and smaller amounts of the shorter-chain homolog **6b** and **6h**, but trace amounts of 6-methylphenanthridine **6g** were also found among the reaction products (see Scheme 3, note *c*).

Discussion

The present synthesis of phenanthridines and related heterocycles entails ring closure by formation of a bond between the α and β carbons of the pyridine ring. Few cases of photoinduced or radical cyclizations to phenanthridines have been reported.[14] In the present context significant similarities can be found in the photocyclization of biphenyl-2-yl isocyanides through imino ether intermediates[15] which method is, however, unsuitable for the preparation of 6-substituted derivatives and in the peroxide-catalyzed cyclization of *N*-(biphenyl-2-yl)arylimines.[16] The photoinduced cyclization of *ortho*-vinyl substituted biaryls (leading primarily to dihydro compounds) is known to require an oxidizing agent. However, in the case of amidines **5** the reaction is completed by virtue of the easy elimination of the morpholino group, directly affording an aromatic product.

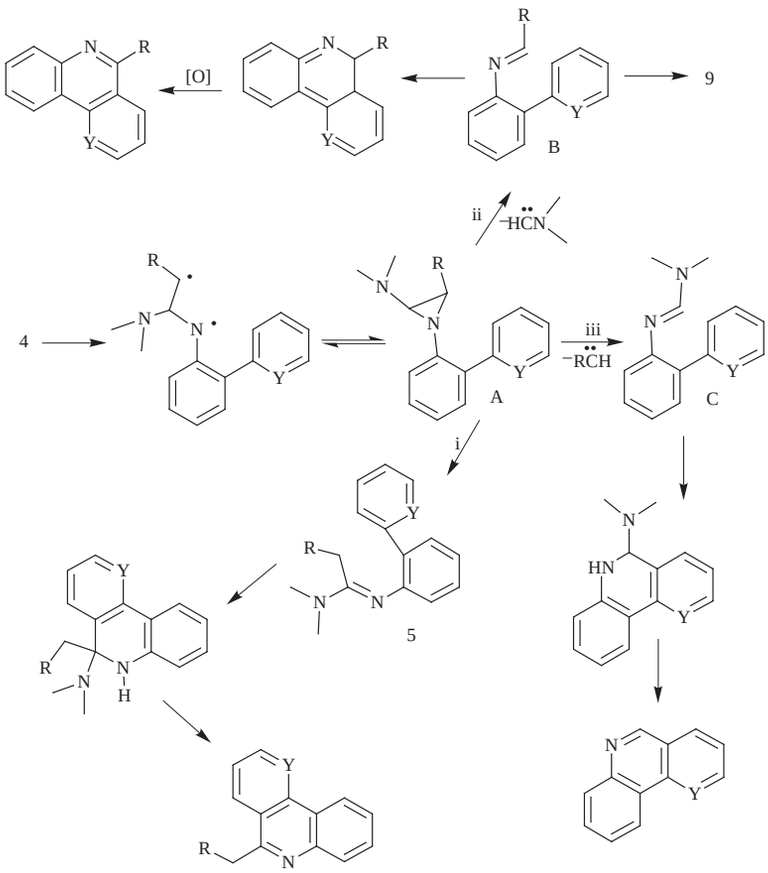
The reaction paths involved in the photoinduced transformations of triazolines **4** are suggested in Scheme 4. Homolytic cleavage of the N1–N2 bond followed by nitrogen elimination affords a diradical intermediate which undergoes reversible cyclization to aziridine **A**. Three reaction paths are now open: (i) the "normal" rearrangement to amidine **5**, (ii) the cycloreversion to imine **B** with elimination of morpholinocarbene, and (iii) the cycloreversion to formamidine **C** with loss of alkylcarbene. The intermediate formation of amidine **5** during the photolysis could be confirmed by TLC. The elimination of carbenic moieties from aziridines under photochemical conditions is precedented.[17] Moreover, path (ii) should be favored over (iii) by virtue of the resonance stabilization of morpholinocarbene.[18] Photocyclization of both **5** and **C** affords the corresponding tricyclic aromatic products through their dihydro derivatives which aromatize by morpholine elimination. Imine **B**, too, eventually affords an aromatic product through cyclization to the corresponding dihydro compound. However, in this case an oxidation step is necessary. The presence of an explicit oxidant is not unavoidable because dihydrophenanthridines are prone to easy spontaneous oxidation. Another possi-



Scheme 3

Starting compounds	Products (yield %, HPLC)			
4a	**6a** (50, 45[a])	**6g**[9] (7[b])	**6h**[10] (2)	**9a** (25)
4b	**6b** (40, 30[a])	**6a** (30, 10[a])	**6h** (3)	**9a** (30, 20[a])
4c	**6c** (15)	**6i**[11] (5)	**6j**[12] (1)	**9b** (25)
4d	**6d** (27)	**6c** (4)	**6j** (1)	**9b** (29)
4e	**6e** (36)	—	**6h** (2)	**9a** (27)
4f	**6f** (33)	**6b** (5)	**6h** (1[c])	**9a** (21)

[a] Isolated yield by chromatography of the crude reaction mixture. [b] The formation of 6-methylphenanthridine **6g** is explained by a subsequent transformation of the main product **6a** through a photolytic fragmentation (of McLafferty type) accompanied by hydrogen transfer and alkene elimination.[13] [c] A trace amount of **6g** was also present.



Scheme 4

bility open to the imine intermediate is hydrolysis to the aldehyde and arylamine **9**. This is also an easy process and this possibility has been confirmed by performing the photolytic reaction of **4a** under carefully anhydrous conditions and in the presence of iodine. In the absence of moisture and in the presence of the oxidising reagent the yield of phenanthridine **6g** was substantially enhanced at the expense of the arylamine **9a**.

From the above, it is concluded that the direct phototransformation of triazolines **4**, though interesting and useful to give a further insight in the chemistry of this class of compounds, can hardly be considered a method of choice to obtain 6-alkylphenanthridines and related heterocycles because the overall yield is only moderate and several by-products are formed. However, the two-step procedure entailing thermal rearrangement of triazolines **4** to amidines **5** followed by photochemical cyclization is satisfactory. Also, the alternative arylation employed for the preparation of compounds **8** is a useful route, mostly when the starting *o*-azidobiaryl is not readily available. The use of amidines instead of simple imines shows practical advantages because imines are rather unstable and, more importantly, the presence of the readily eliminated amino group greatly favors the final outcome of the cyclization step which becomes, in fact, irreversible.

Experimental

Mps were determined by a Büchi 510 (capillary) apparatus. IR spectra were measured with a JASCO IR Report 100 instrument (Nujol or neat). NMR spectra were obtained with Bruker AC 200 and Varian Gemini 200 instruments at 200 MHz. *J* Values are given in Hz for solutions in $CDCl_3$ unless otherwise indicated. HPLC analyses were performed with a Hewlett Packard 1050 liquid chromatograph (Lichrocart 250-4 Superspher 100 RP-18 column, NaH_2PO_4–Na_2HPO_4 0.016 M–MeCN as eluent). 2-Azidobiphenyl,[19] 2-(2-azidophenyl)pyridine,[20] 2-bromophenyl azide[21] and 2-iodophenyl azide[22] are known compounds.

General procedure for the preparation of triazolines 4a–i

To a stirred solution of azide **3** (10 mmol) and aldehyde **1** (11 mmol) in anhydrous toluene (25 mL) morpholine (0.87 g, 10 mmol) was added dropwise at room temperature. Stirring was continued until consumption of the reagents (12–48 h) (reaction monitored by TLC, ethyl acetate–cyclic hexane 2 : 3). Then anhydrous sodium sulfate (1.42 g, 10 mmol) was added and stirring was continued for a few minutes. After filtration the solvent was evaporated to dryness under reduced pressure and diisopropyl ether added until crystallization of the residue occurred. Purification was performed by dissolving in benzene or toluene and reprecipitating with diisopropyl ether or pentane. Mps and analytical data in Table 1.

General procedure for the preparation of amidines 5a–i

The triazoline **4** (10 mmol) was dissolved in anhydrous *p*-xylene (25–30 ml) and heated to reflux until complete transformation of the starting compound as evidenced by TLC (silica gel, ethyl acetate–cyclohexane 2 : 3) (3–5 h). After evaporation of the solvent, the residue was purified by chromatography on a silica gel column with ethyl acetate–cyclohexane 3 : 7 as eluent. After evaporation, the main fraction was triturated with diisopropyl ether. Mps and analytical data in Table 1.

General procedure for the preparation of amidines 5k,l

To a solution of amidines **5g**–**h** (3 mmol) in anhydrous toluene (20 mL) 0.3 mmol of bis(triphenylphosphine)palladium dichloride and 6 mmol of tributyl(2-thienyl)stannane were added. The reaction mixture was heated at reflux, under a nitrogen atmosphere, for 20 h. Then, the toluene solution was evaporated to dryness and the dark residue chromatographed on a

Table 1 Yields, melting points, analytical and ^{1}H NMR data for compounds **4**, **5**, **6**, **8**

Compound (Formula)	Yield (%)	Mp (*T*/°C)	Found (%) (Required) C	H	N	δ_H($CDCl_3$, 200 MHz)
4a ($C_{19}H_{22}N_4O$)	55	137	70.5 (70.8)	6.85 (6.9)	17.6 (17.4)	1.00 (3H, s, Me), 2.00–2.24 and 3.38–3.41 (4 + 4H, 2m, morpholine), 3.36 (1H, d, *J* 2.3, H-5), 4.15 (1H, dq, H-4), 7.31–7.79 (9H, m, ArH)
4b ($C_{20}H_{24}N_4O$)	45	117	71.35 (71.4)	6.9 (7.2)	16.35 (16.65)	0.81 (3H, t, Me), 1.08 and 1.60 (1 + 1H, 2m, CH_2), 1.95–2.20 and 3.35–3.45 (4 + 5H, 2m, morpholine + H-5), 4.02 (1H, dt, H-4), 7.28–7.81 (9H, m, ArH)
4c ($C_{18}H_{21}N_5O$)	50	145	66.65 (66.85)	6.1 (6.55)	21.75 (21.65)	1.04 (3H, s, Me), 2.03–2.27 and 3.33–3.41 (4 + 4H, 2m, morpholine), 3.46 (1H, d, *J* 2.3, H-5), 4.17 (1H, dq, H-4), 7.24–7.48 and 8.73 (7 + 1H, m + d, ArH)
4d ($C_{19}H_{23}N_5O$)	85	125	67.9 (67.65)	6.9 (6.85)	20.5 (20.75)	0.88 (3H, t, Me), 1.15 and 1.61 (1 + 1H, 2m, CH_2), 2.00–2.24 and 3.32–3.41 (4 + 4H, 2m, morpholine), 3.49 (1H, d, *J* 1.8, H-5), 4.08 (1H, dt, H-4), 7.24–7.83 and 8.70 (7 + 1H, m + d, ArH)
4e ($C_{24}H_{24}N_4O$)	55	141	74.7 (74.95)	6.65 (6.3)	14.2 (14.55)	2.05–2.28 and 3.36–3.48 (4 + 4H, 2m, morpholine), 3.60 (1H, d, *J* 2.7, H-5), 5.23 (1H, d, *J* 2.7, H-4), 6.93–7.47 and 7.87 (13 + 1H, m + d, ArH)
4f ($C_{21}H_{26}N_4O$)	65	106	72.05 (71.95)	7.35 (7.5)	15.7 (16.0)	0.88 (3H, t, Me), 1.05–1.65 (2 + 2H, 2m, CH_2CH_2), 1.96–2.19 and 3.35–3.41 (4 + 4H, 2m, morpholine), 3.40 (1H, m, H-5), 4.08 (1H, m, H-4), 7.26–7.45 and 7.77 (8 + 1H, m + d, ArH)
4g ($C_{13}H_{17}IN_4O$)	69	136–137	41.7 (41.95)	4.25 (4.6)	14.8 (15.05)	1.39 (3H, d, Me), 2.18–2.56 and 3.40–3.56 (4 + 4H, 2m, morpholine), 4.42 (1H, dq, H-4), 5.21 (1H, d, H-5), 6.95–7.91 (4H, m, ArH)
4h ($C_{18}H_{19}IN_4O$)	98	131	49.5 (49.8)	4.1 (4.4)	12.75 (12.9)	2.30–2.65 and 3.56–3.67 (4 + 4H, 2m, morpholine), 5.40 and 5.52 (1 + 1H, 2d, H-4 and H-5), 6.96–7.90 (9H, m, ArH)
4i ($C_{13}H_{17}BrN_4O$)	63	130	47.9 (48.0)	4.95 (5.25)	17.65 (17.25)	1.35 (3H, t, Me), 2.20–2.52 and 3.42–3.50 (4 + 4H, 2m, morpholine), 4.42 (1H, dq, H-4), 5.12 (1H, d, H-5), 7.10–7.73 (4H, m, ArH)
5a ($C_{19}H_{22}N_2O$)	70	83	77.4 (77.5)	7.35 (7.5)	9.45 (9.5)	0.76 (3H, t, Me), 2.01 (2H, q, CH_2), 3.36–3.40 and 3.61–3.65 (4 + 4H, 2m, morpholine), 6.77 and 7.19–7.48 (1 + 8H, 2m, ArH)
5b ($C_{20}H_{24}N_2O$)	50	108	77.6 (77.9)	7.65 (7.85)	9.0 (9.1)	0.70 (3H, t, Me), 1.21 and 1.91 (2 + 2H, 2m, CH_2CH_2), 3.34–3.38 and 3.59–3.64 (4 + 4H, 2m, morpholine), 6.76 and 7.01–7.47 (1 + 8H, d + m, ArH)
5c ($C_{18}H_{21}N_3O$)	45	82	73.0 (73.2)	6.85 (7.15)	14.0 (14.25)	0.72 (3H, t, Me), 2.05 (2H, q, CH_2), 3.40–3.45 and 3.64–3.68 (4 + 4H, 2m, morpholine), 6.76, 7.06–7.74 and 8.64 (1 + 6 + 1H, d + m + d, ArH)
5d ($C_{19}H_{23}N_3O$)	60	Oil	73.85 (73.75)	7.8 (7.5)	13.25 (13.6)	0.70 (3H, t, Me), 1.08–1.46 and 1.94–2.34 (2 + 2H, 2m, CH_2CH_2), 3.39–3.47 and 3.58–3.68 (4 + 4H, 2m, morpholine), 6.75, 6.80–7.73 and 8.65 (1 + 6 + 1H, d + m + d, ArH)
5e ($C_{24}H_{24}N_2O$)	22	124	80.65 (80.85)	6.45 (6.8)	7.7 (7.85)	3.32–3.37 and 3.46–3.50 (4 + 4H, 2m, morpholine), 3.41 (2H, s, CH_2), 6.8–7.52 (14H, m, ArH)
5f ($C_{21}H_{26}N_2O$)	68	Oil	77.95 (78.2)	7.95 (8.15)	8.45 (8.7)	0.71 (3H, t, Me), 1.02–1.19 [4H, m, (Me)CH_2CH_2], 1.96 (2H, t, CH_2), 3.32–3.34 and 3.60–3.64 (4 + 4H, 2m, morpholine), 6.75 and 7.01–7.50 (1 + 8H, d + m, ArH)
5g ($C_{13}H_{17}IN_2O$)	78	Oil	45.0 (45.35)	5.15 (5.0)	8.25 (8.15)	1.01 (3H, t, Me), 2.19 (2H, q, CH_2), 3.51–3.62 and 3.73–3.87 (4 + 4H, 2m, morpholine), 6.62–7.83 (4H, m, ArH)
5h ($C_{18}H_{19}IN_2O$)	24	100	53.4 (53.2)	4.5 (4.7)	6.6 (6.9)	3.50–3.70 (10H, m, morpholine and CH_2), 6.60–7.80 (9H, m, ArH)
5i ($C_{13}H_{17}BrN_2O$)	68	Oil	52.2 (52.55)	5.45 (5.75)	9.3 (9.45)	1.01 (3H, t, Me), 2.19 (2H, q, CH_2), 3.74–3.79 (4 + 4H, 2m, morpholine), 6.70–7.56 (4H, m, ArH)
5j ($C_{15}H_{20}N_2O$)	36	Oil	73.6 (73.75)	8.0 (8.25)	11.15 (11.45)	0.92 (3H, t, Me), 2.17 (2H, q, CH_2), 3.75–3.79 (4 + 4H, 2m, morpholine), 5.15, 5.63 and 6.65 (1 + 1 + 1H, ABX-system, *J* 11.1, 17.8 and 9.0, CH=CH_2), 6.73–7.51 (4H, m, ArH)
5k ($C_{17}H_{20}N_2OS$)	48	Oil	67.75 (67.95)	6.6 (6.7)	9.1 (9.3)	0.89 (3H, t, Me), 2.20 (2H, q, CH_2), 3.58–3.69 and 3.75–3.82 (4 + 4H, 2m, morpholine), 6.68–7.73 (7H, m, ArH)
5l ($C_{22}H_{22}N_2OS$)	26	121	72.65 (72.9)	5.95 (6.1)	7.85 (7.75)	3.53–3.70 (10H, m, morpholine and CH_2), 6.70–7.77 (12H, m, ArH)
6a ($C_{15}H_{13}N$)	78	59 (lit.,[9] 56)				1.53 (3H, t, Me), 3.44 (2H, q, CH_2), 7.63–7.88 (4H, m, H-2, H-3, H-8, H-9), 8.12, 8.27, 8.55 and 8.63 (1 + 1 + 1 + 1H, 4dd, H-1, H-4, H-7, H-10)
6b ($C_{16}H_{15}N$)	71	Oil (lit.,[23] bp 228/22)				1.13 (3H, t, Me), 2.01 [2H, q, CH_2(Me)], 3.36 (2H, t, CH_2), 7.58–7.89 (4H, m, H-2, H-3, H-8, H-9), 8.13, 8.27, 8.55 and 8.65 (1 + 1 + 1 + 1H, 4dd, H-1, H-4, H-7, H-10)
6c ($C_{14}H_{12}N_2$)	88	86	80.5 (80.75)	5.65 (5.8)	13.3 (13.45)	1.51 (3H, t, Me), 3.40 (2H, q, CH_2), 7.60–7.86 (3H, m, H-3, H-8, H-9), 8.13 (1H, dd, H-4), 8.53 (1H, dd, H-10), 9.05–9.18 (2H, m, H-2 and H-7)
6d ($C_{15}H_{14}N_2$)	85	Oil	80.9 (81.05)	6.0 (6.35)	12.35 (12.6)	1.13 (3H, t, Me), 1.95 [2H, q, CH_2(Me)], 3.33 (2H, t, CH_2), 7.60–7.87 (3H, m, H-3, H-8, H-9), 8.14, 8.54 and 9.18 (1 + 1 + 2H, 2dd + m, H-4, H-10 and H-7, H-2)
6e ($C_{20}H_{15}N$)	70	111 (lit.,[9] 112–113)				
6f ($C_{17}H_{17}N$)	70	Oil (lit.,[24] bp 182–184)	86.8 (86.75)	7.0 (7.3)	5.8 (5.95)	1.01 (3H, t, Me), 1.45–1.67 and 1.80–2.05 [2 + 2H, 2m, CH_2CH_2(Me)], 3.38 (2H, t, CH_2), 7.55–7.90 (4H, m, H-2, H-3, H-8, H-9), 8.13, 8.27, 8.55 and 8.65 (1 + 1 + 1 + 1H, 4dd, H-1, H-4, H-7, H-10)
8a ($C_{13}H_{11}NS$)	44	81	72.9 (73.2)	5.4 (5.2)	6.35 (6.55)	1.49 (3H, t, Me), 3.29 (2H, q, CH_2), 7.51–7.75 and 8.03–8.20 (4 + 2H, 2m, ArH)
8b ($C_{18}H_{13}NS$)	54	95	78.4 (78.5)	4.4 (4.75)	5.2 (5.1)	4.63 (2H, s, CH_2), 7.14–7.75 and 8.05–8.27 (9 + 2H, 2m, ArH)

silica gel column with ethyl acetate–cyclohexane 15:85 as eluent. Pure **5k** was obtained as an oily compound and **5l** as a brown solid compound crystallized from diisopropyl ether. Analytical data in Table 1.

General procedure for the cyclization of amidines 5a–f,k,l

The amidine **5** (10 mmol) was dissolved in anhydrous benzene (300 mL) and irradiated with a high-pressure Hg lamp, with

Pyrex filter, until reaction was complete (6–10 h), as confirmed by TLC (silica gel, ethyl acetate–cyclohexane 3 : 7). The solvent was evaporated and the residue purified by chromatography on a silica gel column with ethyl acetate–cyclohexane 3 : 7 as eluent affording pure **6** and **8a**,**b**. Physical and analytical data in Table 1.

(2-Vinylphenyl)(1-morpholin-4-ylpropylidene)amine 5j

To a solution of 1.48 g (5 mmol) of amidine **5i** in anhydrous toluene (15 mL) 0.577 g (0.05 mmol) of tetrakis(triphenylphosphine)palladium and 1.74 g (55 mmol) of tributyl(vinyl)-stannane were added. The reaction mixture was heated at reflux, under a nitrogen atmosphere, for 8 h. Then, the dark reaction solution was evaporated to dryness and the residue chromatographed on a silica gel column with ethyl acetate–cyclohexane 3 : 7 as eluent. Pure **5j** was obtained as an oily compound. Data in Table 1.

2-Ethylquinoline 7

A solution of 0.98 g (4 mmol) of amidine **5j** in anhydrous benzene (200 mL) was irradiated with a high-pressure Hg lamp, with Pyrex filter, until reaction was complete (10 h), as confirmed by TLC (silica gel, ethyl acetate–cyclohexane 3 : 7). The solvent was evaporated and the residue purified by chromatography on a silica gel column with ethyl acetate–cyclohexane 1 : 4 as eluent affording pure **7** (yield 62%, oil, lit.[25]).

General procedure for the photolysis of triazolines 4a–f

To a solution of triazoline **4** (2 mmol) in anhydrous benzene a small iodine crystal was added and the solution was irradiated with a high-pressure Hg lamp, with Pyrex filter, until complete transformation of the starting product (10–18 h), as confirmed by TLC (silica gel, ethyl acetate–cyclohexane 3 : 7). The solvent was evaporated and the residue was analyzed by HPLC. The products formed with their relative yields are listed in Scheme 3. The crude reaction mixture was chromatographed on a silica gel column with hexane–dichloromethane 3 : 1 as eluent, affording pure samples of the main products as indicated in Scheme 3.

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