# *v*-Triazolines. Part 38.[1] New synthesis of 4-aminoquinazolines and 6-aminopurines

**Emanuela Erba * and Daniela Sporchia**

*Istituto di Chimica Organica, Facoltà di Farmacia, Università degli Studi di Milano, Via Venezian, 21, I-20133 Milano*

**2-Alkyl-4-arylaminoquinazolines 6 have been prepared by condensation of *N*-(2-cyanophenyl)amidines 5 with arylamines. The amidines 5 were obtained by thermal rearrangement of *N*-(2-cyanophenyl)-5-morpholino-*v*-triazolines 4. The synthesis has been applied to the preparation of 2-alkyl-6-arylaminopurines 12.**



## Introduction

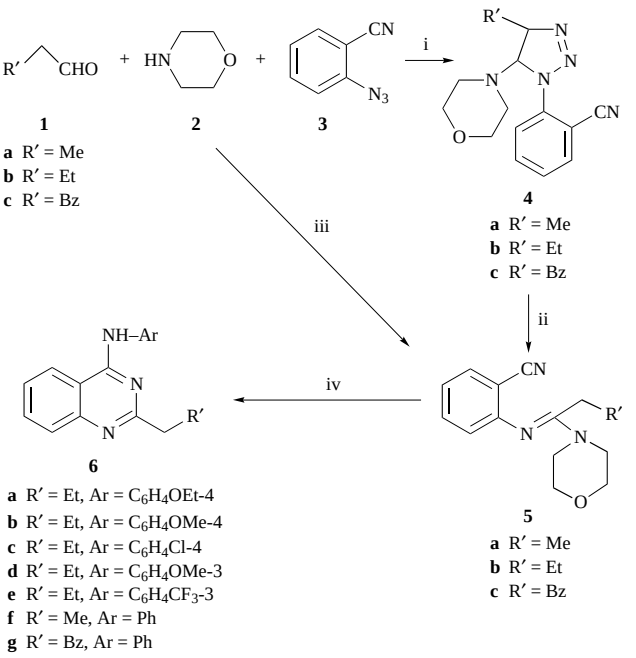
Previous papers from our research group have been concerned with the synthetic use of 5-amino-4,5-dihydro-*v*-triazoles as versatile precursors of N-containing heterocycles. A major advantage of using triazolines resides in their ready availability by 1,3-dipolar cycloaddition of enamines and azides which, in most instances, can be performed by a very simple procedure entailing the direct three-component reaction of an aldehyde (or ketone), an aliphatic secondary amine and an aryl azide. Several transformation paths are known for the 5-amino-*v*-triazoline ring,[2] but the most studied and synthetically useful is the thermally induced elimination of nitrogen accompanied by rearrangement to tertiary amidines. In the past, we found straightforward routes to N-containing heterocycles by combining the synthesis of triazolines, their rearrangement to amidines and appropriate transformations of the latter.[1,3]

As a further development in this field, we now report a new and easy synthesis of 2-alkyl-4-amino- and -4-arylaminoquinazolines which can be successfully applied also to the preparation of medicinally interesting 2-alkyladenines and their 6-*N*-aryl derivatives.

## Results and discussion

Reaction of an aldehyde **1a**–**c** with morpholine **2** and 2-azidobenzonitrile **3** in benzene at room temperature readily afforded the corresponding triazolines **4a**–**c** (in the *trans* configuration) by cycloaddition of the azide to the intermediate enamines (see Scheme 1). Compounds **4** when heated in boiling *p*-xylene gave the corresponding amidines **5a**–**c**. Cleavage of the N(1)–N(2) bond is made easier by virtue of the electron-withdrawing effect of the electron-poor substituent on N-1; nitrogen elimination and hydrogen migration then follow. As expected, compounds **5** could be obtained directly when the starting materials were allowed to react at an elevated temperature.

The amidines **5a**–**c** underwent cyclocondensation with primary arylamines to give the corresponding 2-alkyl-4-arylaminoquinazolines **6a**–**g** (Scheme 1), although relatively high temperatures and the presence of an acid (in the form of amine salt or free organic acid) were necessary. Preferably, the acid was used in at least equimolar amount, which is justified by the basicity of the products **6**, obtained as salts. Two condensation techniques were applied, with similar results in most cases: (i) heating of the amidine **5** with an equimolar amount of arylamine hydrochloride without solvent in a sealed bomb or (ii) refluxing of the arylamine and the amidine **5** in an organic acid, preferably propionic acid. In this latter case use of an excess of the aniline reactant was advantageous because some propionanilide was unavoidably formed as a by-product.

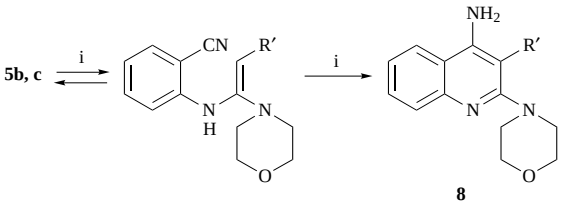



**Scheme 1** *Reagents and conditions:* i, $CHCl_3$, RT, 4 h; ii, *p*-xylene, reflux, 3 h; iii, *p*-xylene, reflux, 4 h; iv, $ArNH_2$·HCl, 180 °C, 2 h or $ArNH_2$, $EtCO_2H$, reflux, 2 h

The structures of compounds **6a**–**g** were established on the basis of IR and $^1H$ and $^{13}C$ NMR data. Although tautomeric forms of these compounds are possible, this aspect was not studied in detail. However, the $^{15}N$ NMR spectrum of **6b** shows a signal at $\delta$ 306 associated with the NH group which is typical of a diarylamine[4] suggesting the predominance of the aromatic quinazoline form, at least in solution.

The condensation leading to compounds **6** is understandable in terms of an acid-catalyzed addition of arylamine to the nitrile group, followed by ring-closure and the elimination of morpholine. The low yields of the quinazoline product obtained for **6c** and **6e** even when longer reaction times were used, is explained by the lower nucleophilicity of the substituted arylamines. In both cases, besides the expected aminoquinazoline, 2-propyl-4-quinazolone **7** was isolated as the result of hydrolysis. A slightly different result was obtained with 3-phenylpropionamidine **5c** when the expected 2-phenylethylquinazoline **6g** was accompanied by a substantial amount of 4-amino-3-benzyl-2-morpholinoquinoline **8b**, generated probably

by competitive acid-catalyzed tautomerization of the amidine followed by intramolecular addition of the enamine carbon to the nitrile group (Scheme 2). This mechanism was confirmed



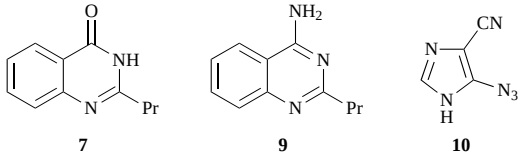

**8**

**a** R′ = Et
**b** R′ = Bz

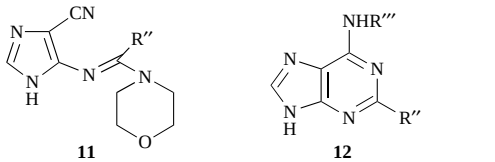
**Scheme 2** *Reagents and conditions:* i, $PhNEt_2$·HCl, 180 °C, 2 h

by treating the amidines **5b**,**c** with *N*,*N*-diethylaniline hydrochloride when with acidic catalysis, but in the absence of primary amine, both compounds produced the corresponding quinolines **8a**,**b** as the sole reaction products.

The condensation of the amidines **5** with aliphatic amines gave low yields of final products. However, reaction of the amidine **5b** with ammonium acetate afforded a 40% yield of 4-amino-2-propylquinazoline **9**. The above synthesis was successful for the preparation of other heterocycles containing a condensed pyrimidine ring; thus, the adenine derivatives **12a**–**c** were obtained by the reaction of 4-methoxyaniline or




**7** **9** **10**




**11** **12**

**a** R″ = Et
**b** R″ = Pr

**a** R″ = Et, R‴ = $C_6H_4OMe$-4
**b** R″ = Pr, R‴ = $C_6H_3(OMe)_2$-3, 4
**c** R″ = Pr, R‴ = H

3,4-dimethoxyaniline with the amidines **11a**,**b** in the presence of ammonium acetate. The amidines **11a**,**b** were obtained from 4-azido-5-cyanoimidazole[5] **10**, the aldehydes **1a**,**b** and morpholine.

In conclusion, the thermal rearrangement of 5-amino-*v*-triazolines is the method of choice for the easy and straightforward preparation of functionalized amidines which are, in turn, precursors of substituted N-heterocycles.

## Experimental

Mps were determined using a Büchi 510 capillary apparatus. IR spectra were measured using a JASCO IR Report 100 instrument. NMR spectra were obtained with Bruker AC 200 and EM-390 Varian instruments. Column chromatography was performed on silica gel with Kieselgel 60–70, 230 ASTM. 2-Azidobenzonitrile **3**[6] and 5-azido-3-cyanoimidazole **10**[5] are known compounds.

### General procedure for the preparation of 2-(4-alkyl-4,5-dihydro-5-morpholino-1*H*-1,2,3-triazol-1-yl)benzonitriles 4a–c

The azide **3** (35 mmol) and the aldehyde **1a**–**c** (52 mmol) were dissolved in $CHCl_3$ (40 ml) to which morpholine (52 mmol) was then added dropwise. The reaction mixture was stirred at room temperature for 4 h after which it was dried ($Na_2SO_4$) and concentrated under reduced pressure. The residue was recrystallized to afford the triazolines **4a**–**c**, the analytical and spectral data for which are listed in Table 1.

### General procedure for the preparation of 2-(2-alkylethylidenamino-1-morpholino)benzonitriles 5a–c

The azide **3** (35 mmol) and the aldehyde **1a**–**c** (52 mmol) were dissolved in *p*-xylene (40 ml) and morpholine (52 mmol) were added dropwise to the solution. The mixture was then refluxed for 5 h until disappearance of starting material [TLC, ethyl acetate–cyclohexane (2:3)]. The crude reaction mixture was dried ($Na_2SO_4$) and concentrated under reduced pressure and the residue was recrystallized. Analytical and spectral data are listed in Table 1.

### General procedure for the preparation of 5-(1-morpholinoalkylamino)-1*H*-imidazole-4-carbonitriles 11a,b

The azide **10** (8 mmol) and the aldehyde **1a**,**b** (8 mmol) were dissolved in toluene (10 ml) to which morpholine (8 mmol) was then added dropwise. The reaction mixture was stirred at room temperature for 14 h after which it was dried ($Na_2SO_4$) and concentrated under reduced pressure. The residue was chromatographed with ethyl acetate. Analytical data are listed in Table 1.

### General procedure for the preparation of (2-alkylquinazolin-4-yl)-arylamines 6a–g

**Method A.** The arylamine (8.1 mmol) was dissolved in propionic acid (10 ml) and amidine **5a**–**c** (6.7 mmol) was added to the solution. This was then refluxed for 2 h until disappearance of starting material [TLC, ethyl acetate–cyclohexane (2:3)]. After evaporation of most of the propionic acid, the residue was dissolved in $CH_2Cl_2$ and the solution first washed with aqueous $NaHCO_3$ and then thrice extracted with 1 M aqueous HCl. The acid solution was washed with diethyl ether, basified at pH 8 with $Na_2CO_3$ and extracted with diethyl ether. After evaporation the crude reaction mixture was crystallized or purified by chromatography with ethyl acetate–cyclohexane (3:7). Analytical and spectral data are listed in Table 1.

**Method B.** The arylamine hydrochloride (4.6 mmol) and the amidine **5** (5.5 mmol) mixed and sealed in a bomb (vol. 2 ml) were heated in a bath at 180 °C for 2 h. The residue was taken up with $CH_2Cl_2$ and the solution washed with aqueous $NaHCO_3$, dried ($Na_2SO_4$) and evaporated under reduced pressure. The crude residue was purified by chromatography with ethyl acetate–cyclohexane (3:7). Analytical and spectral data are listed in Table 1.

### General procedure for the preparation of (2-alkyl-9*H*-purin-6-yl)-arylamines 12a–c

The arylamine hydrochloride (3 mmol) and the amidine **11a**,**b** (2 mmol) mixed and sealed in a bomb (vol. 2 ml) were heated in a bath at 180 °C for 2 h. The residue was taken up with $CH_2Cl_2$ (20 ml) and water (20 ml) and basified with aqueous $NaHCO_3$. The insoluble product was filtered off and recrystallized. Analytical and spectral data are listed in Table 1.

### Preparation of 3-alky-4-amino-2-morpholinoquinolines 8a,b

Diethylphenylamine hydrochloride (4.6 mmol) mixed with the amidines **5b**,**c** (5.5 mmol) in a sealed bomb (vol. 2 ml), were heated in a bath at 180 °C for 2 h. The residue was taken up with $CH_2Cl_2$ and the solution washed with aqueous $NaHCO_3$, dried ($Na_2SO_4$) and evaporated to dryness under reduced pressure. The crude residue was purified by chromatography [ethyl acetate–cyclohexane (2:3)]. Analytical and spectral data are listed in Table 1.

### Preparation of (2-propylquinazolin-4-yl)amine 9 and (2-propyl-9*H*-purin-6-yl)amine 12c

The amidine **5b** or **11b** (5 mmol) and $NH_4CO_2Me$ (50 mmol) mixed and sealed in a bomb (vol. 2 ml) were heated in a bath at

**Table 1**

| Compound (Formula) | Yield (%) [method] | Mp ($T$/°C) [solv.] | $\nu_{max}$/cm$^{-1}$ (Nujol) | $\delta_H$($J$/Hz)[a] | Found (%) (requires) C | H | N |
|---|---|---|---|---|---|---|---|
| **4a** ($C_{14}H_{17}N_5O$) | 85 | 119 [Pr$^i_2$O] | 2200 (CN) | 1.32 (3H, d, $J$ 7.2, $CH_3$), 2.21–2.39 (4H, m, $CH_2NCH_2$), 3.37–3.55 (4H, m, $CH_2OCH_2$), 4.56 (1H, dq, $J$ 2.28 and 7.2, H-4), 5.19 (1H, d, $J$ 2.28, H-5), 7.17 (1H, d, $J$ 8.00 and 1.02, H-3′), 7.52–7.63 (2H, m, H-2′ and H-4′), 7.98 (1H, dd, $J$ 8.00 and 1.02, H-5′) | 61.7 (62.0) | 6.5 (6.3) | 25.4 (25.8) |
| **4b** ($C_{15}H_{19}N_5O$) | 56 | 83 [Pr$^i_2$O] | 2200 (CN) | 0.82 (3H, t, $J$ 7.36, $CH_3$), 1.27–1.58 (2H, m, $CH_2CH_3$), 2.18–2.26 (2H, m, $CH_2CH_2$), 3.53–3.58 (4H, m, $CH_2NCH_2$), 3.73–3.78 (4H, m, $CH_2OCH_2$), 6.77 (1H, dd, $J$ 7.8 and 1.06, H-5′), 6.97 (1H, dt, $J$ 7.8 and 1.06, H-3′), 7.42 (1H, dt, $J$ 7.8 and 1.43, H-4′), 7.51 (1H, dd, $J$ 7.8 and 1.43, H-2′) | 62.8 (63.1) | 6.9 (6.7) | 24.2 (24.6) |
| **4c** ($C_{20}H_{21}N_5O$) | 65 | 108 [Pr$^i_2$O] | 2200 (CN) | 1.93–2.17 (4H, m, $CH_2NCH_2$), 2.50–2.2 (1H, m, CH benzylic), 3.25–3.48 (5H, m, $CH_2OCH_2$ and 1H benzylic), 4.72–4.80 (1H, m, H-4), 5.26 (1H, d, $J$ 2.52, H-5) and 7.16–7.89 (9H, m, arom.) | 68.95 (69.2) | 6.5 (6.1) | 19.9 (20.2) |
| **5a** ($C_{14}H_{17}N_3O$) | 85 | Oil | 2200 (CN) | 1.06 (3H, t, $J$ 7.69, $CH_3$), 2.27 (2H, q, $CH_2$, $J$ 7.69), 3.51–3.59 (4H, m, $CH_2NCH_2$), 3.74–3.79 (4H, m, $CH_2OCH_2$), 6.79 (1H, d, $J$ 7.88, H-5′), 6.98 (1H, t, $J$ 7.88, H-3′), 7.43 (1H, dt, $J$ 7.88 and 1.38, H-4′), 7.52 (1H, dd, $J$ 7.88 and 1.38, H-2′) | 68.9 (69.1) | 7.4 (7.05) | 17.07 (17.3) |
| **5b** ($C_{15}H_{19}N_3O$) | 52 | 83 [Pr$^i_2$O] | 2200 (CN) | 0.82 (3H, t, $J$ 7.36, $CH_3$), 1.27–1.58 (2H, m, $CH_2CH_3$), 2.18–2.26 (2H, m, $CH_2CH_2$), 3.53–3.58 (4H, m, $CH_2NCH_2$), 3.73, 3.78 (4H, m, $CH_2OCH_2$), 6.77 (1H, dd, $J$ 7.8 and 1.06, H-5′), 6.97 (1H, dt, $J$ 7.8 and 1.06, H-3′), 7.42 (1H, dt, $J$ 7.8 and 1.43, H-4′), 7.51 (1H, dd, $J$ 7.8 and 1.43, H-2′) | 69.85 (70.1) | 7.8 (7.45) | 16.1 (16.35) |
| **5c** ($C_{20}H_{21}N_3O$) | 52 | 75.6 [EtOH] | 2200 (CN) | 2.52–2.78 (4H, m, $CH_2CH_2$), 3.54–3.59 (4H, m, $CH_2NCH_2$), 3.71–3.75 (4H, m, $CH_2OCH_2$), 6.59–7.55 (9H, m, arom.) | 75.1 (75.2) | 6.9 (6.6) | 12.95 (13.2) |
| **6a**[b] ($C_{19}H_{21}N_3O$) | 60 [B] | 176 [Pr$^i_2$O] | 3200 (NH) | 1.03 (3H, t, $J$ 7.53, $CH_3CH_2$), 1.44 (3H, t, $J$ 6.96, $CH_3CH_2O$), 1.91 (2H, sext, $J$ 7.53, $CH_2CH_2$), 2.88 (2H, t, $J$ 7.53, $CH_2CH_2$), 4.07 (2H, q, $J$ 6.96, $CH_2O$) 6.93–7.87 (8H, m, arom.) and 7.29 (1H, br s, NH) | 74.05 (74.3) | 7.1 (6.9) | 13.4 (13.6) |
| **6b** ($C_{18}H_{19}N_3O$) | 65 [A] | 188 [Pr$^i_2$O] | 3200 (NH) | 1.03 (3H, t, $J$ 7.40, $CH_3$), 1.92 (2H, sext, $J$ 7.40, $CH_2$), 2.84 (2H, t, $J$ 7.40, $CH_2CH_2$), 3.84 (3H, s, $OCH_3$), 6.95 (2H, d, $J$ 9.08, H-3′ and H-5′), 7.38 (1H, br s, NH), 7.46 (1H, dt, $J$ 8.1 and 1.35, H-6), 7.72 (2H, d, $J$ 9.08, H-2′ and H-6′), 7.77–7.87 (3H, m, H-5 and H-7 and H-8) | 73.7 (73.8) | 6.7 (6.5) | 14.25 (14.3) |
| **6c** ($C_{17}H_{16}ClN_3$) | 25 [A] 20 [B] | 196 [Pr$^i$OH] | 3275 (NH) | 0.97 (3H, t, $J$ 7.54, $CH_3$), 1.86 (2H, sext, $J$ 7.54, $CH_2CH_3$), 2.83 (2H, t, $J$ 7.54, $CH_2CH_2$), 7.29 (2H, d, $J$ 8.95, H-3′ and H-5′), 7.38–8.54 (4H, m, arom.), 7.86 (2H, d, $J$ 8.95, H-2′ and H-4′) and 8.54 (1H, br s, NH) | 68.7 (68.6) | 5.8 (5.4) | 14.0 (14.1) |
| **6d** ($C_{18}H_{19}N_3O$) | 38 [A] | 105.5 [Pr$^i_2$O] | 3275 (NH) | 1.04 (3H, t, $J$ 7.40, $CH_3$), 1.97 (2H, sext, $J$ 7.40, $CH_2CH_3$), 2.93 (2H, t, $J$ 7.40, $CH_2CH_2$), 3.87 (3H, s, $OCH_3$), 6.68–7.89 (8H, m, arom.), 7.48 (1H, br s, NH) | 73.6 (73.8) | 6.7 (6.5) | 14.2 (14.3) |
| **6e** ($C_{18}H_{16}F_3N_3$) | 15 [B] | 170 [Pr$^i_2$O] | 3250 (NH) | 1.04 (3H, t, $J$ 7.40, $CH_3$), 1.98 (2H, sext, $J$ 7.40, $CH_2CH_3$), 2.94 (2H, t, $J$ 7.40, $CH_2CH_2$, 7.37–8.38 (8H, m, arom.) and 7.63 (1H, br s, NH) | 65.1 (65.3) | 5.1 (4.9) | 12.6 (12.7) |
| **6f** ($C_{16}H_{15}N_3$) | 45 [A] | 189 [Pr$^i_2$O] | 3200 (NH) | 1.44 (3H, t, $J$ 7.57, $CH_3$), 2.97 (2H, q, $J$ 7.57, $CH_2$), 7.12–7.89 (9H, m, arom.), 7.46 (1H, br s, NH) | 77.05 (77.2) | 6.4 (6.1) | 16.7 (16.9) |
| **6g** ($C_{22}H_{19}N_3$) | 30 [A] | 141 [EtOH] | 3200 (NH) | 3.27 (4H, s, $CH_2CH_2$), 7.12–7.94 (14H, m, arom.), 7.79 (1H, br s, NH) | 81.0 (81.2) | 6.1 (5.9) | 12.6 (12.9) |
| **8a**[c] ($C_{15}H_{19}N_3O$) | 25 | 158 [Pr$^i$OH] | 3450 3550 ($NH_2$) | 1.26 (3H, t, $J$ 7.50, $CH_3$), 2.78 (2H, q, $J$ 7.50, $CH_2$), 3.22 (4H, m, $CH_2NCH_2$), 3.90 (4H, m, $CH_2OCH_2$), 4.57 (2H, br s, $NH_2$), 7.29–7.84 (4H, m, arom.) | 69.8 (70.0) | 7.6 (7.4) | 16.05 (16.3) |
| **8b** ($C_{20}H_{21}N_3O$) | 28 | 168 [EtOH] | 3450 3550 ($NH_2$) | 3.15–3.29 (4H, m, $CH_2NCH_2$), 4.75–4.90 (4H, m, $CH_2OCH_2$), 4.20 (2H, s, $CH_2Ph$), 4.44 (2H, br s, $NH_2$) and 7.15–7.85 (9H, m, arom.) | 74.9 (75.2) | 6.8 (6.6) | 13.0 (13.15) |
| **9** ($C_{11}H_{13}N_3$) | 45 | 213 [Pr$^i$OH] | 3050 3250 ($NH_2$) | 0.93 (3H, t, $J$, 7.57, $CH_3$), 1.77 (2H, sext, $J$ 7.57, $CH_2CH_3$), 2.65 (2H, t, $J$ 7.57, $CH_2CH_2$), 7.37–8.19 (4H, m, arom.) and 7.67 (2H, br s, $NH_2$) | 70.20 (70.58) | 7.0 (6.95) | 22.2 (22.4) |
| **11a** ($C_{11}H_{15}N_5O$) | 60 | Oil | 2200 (CN) | 1.12 (3H, t, $J$ 7.52, $CH_3$), 2.48 (2H, q, $J$ 7.52, $CH_2$), 3.52–3.79 (8H, m, morpholine) and 7.35 (1H, s, H-2) | 56.2 (56.6) | 6.7 (6.5) | 29.8 (30.0) |
| **11b** ($C_{12}H_{17}N_5O$) | 58 | Oil | 2200 (CN) | 0.96 (3H, t, $J$ 7.50, $CH_3$), 1.45–1.72 (2H, m, $CH_2$), 2.45–2.53 (2H, m, $CH_2$), 3.60–3.78 (8H, m, morpholine) and 7.44 (1H, s, H-2) | 58.0 (58.3) | 7.0 (6.9) | 28.1 (28.3) |
| **12a**[d] ($C_{14}H_{15}N_5O\cdot H_2O$) | 37 | 272 [$H_2O$] | 3250 (NH) | 1.30 (3H, t, $J$. 7.6, $CH_3$), 2.76 (2H, q, $J$ 7.6, $CH_2$), 3.75 (3H, s, $OCH_3$), 6.90 (2H, d, $J$ 8.9, H-3′ and H-5′), 7.92 (2H, d, $J$ 8.9, H-2′ and H-5′), 8.09 (1H, s, H-2), 9.58 (1H, br s, NH–Ar) | 58.1 (58.5) | 5.4 (5.6) | 24.1 (24.4) |
| **12b** ($C_{16}H_{19}N_5O_2$) | 29 | 239 [$CH_3CN$] | 3250 (NH) | 1.06 (3H, t, $J$ 7.55, $CH_3$), 1.98–2.18 (2H, m, $CH_2$), 2.92–3.06 (2H, m, $CH_2$), 3.90 and 3.96 (6H, 2 s, $OCH_3$), 6.89 (1H, d, $J$ 8.8, H-3′), 7.19 (1H, dd, $J$ 8.8 and 2.2, H-2′), 7.73 (1H, br s, NHAr), 7.85 (1H, d, $J$ 2.2, H-6′), 7.95 (1H, s, H-2) | 51.4 (51.75) | 6.4 (6.1) | 22.1 (22.3) |
| **12c** ($C_8H_{11}N_5\cdot HCl$) | 35 | 206–7 [MeOH] | 3250–3050 ($NH_2$) | 0.93 (3H, t, $J$ 7.3, $CH_3$), 1.72–1.82 (2H, m, $CH_2$), 2.52–2.61 (2H, t, $J$ 7.6, $CH_2$), 6.95 (2H, br s, $NH_2$) | 44.7 (45.0) | 5.3 (5.2) | 32.5 (32.8) |

[a] $CDCl_3$; DMSO for **9** and **12c**. [b] $\delta_C$(DMSO) 13.75 (q), 20.89 (t), 41.00 (q), 55.01 (q), 119.83 (d), 128.34 (d), 128.90 (d), 130.36 (d), 132.63 (d), 137.64 (s), 137.95 (s), 155.27 (s), 157.49 (s) and 165.78 (s); $\delta_N$(DMSO) 306.2 (NH). [c] $\delta_C$($CDCl_3$) 12.87 (q), 19.84 (t), 52.96 (t), 67.79 (t), 110.87 (s), 117.96 (s), 120.12 (d), 123.88 (d), 128.97 (d), 146.53 (s), 148.53 (s) and 162.41 (s). [d] $\delta_C$(DMSO) 18.28 (q), 37.36 (t), 60.41 (t), 97.80 (d), 118.85 (d), 121.44 (s), 126.83 (d), 138.35 (s), 156.1 (s), 158.52 (s), 159.70 (s) and 169.41 (s).

180 °C for 2 h. The residue was taken up with $CH_2Cl_2$, washed with aqueous $NaHCO_3$, dried ($Na_2SO_4$) and evaporated to dryness. The residue was purified by chromatography **9** or recrystallized from water (**12c**). Analytical and spectral data are listed in Table 1.

## Acknowledgements

This work has been supported by M.U.R.S.T.

## References

1 Part 37. E. M. Beccalli, E. Erba, M. L. Gelmi and D. Pocar, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 1359.
2 P. Kadaba, S. Stanovnik and M. Tisler, *Adv. Heterocycl. Chem.*, 1984, **37**, 329 and references cited therein.
3 R. Angelini, E. Erba and D. Pocar, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 837; M. Battistini, E. Erba and D. Pocar, *Synthesis*, 1992, 1206; M. Battistini, E. Erba and D. Pocar, *J. Chem. Soc.*, *Perkin Trans. 1*, 1993, 339; E. Erba, G. Mai and D. Pocar, *J. Chem. Soc.*, *Perkin Trans. 1*, 1992, 2709.
4 G. J. Martin, M. L. Martin and J. P. Goucsnard, *$^{15}$N-NMR Spectroscopy*, Springer-Verlag, Berlin, 1981, 126.
5 A. P. Freitas, M. F. J. R. P. Proença and B. L. Booth, *J. Heterocycl. Chem.*, 1995, **32**, 457.
6 M. O. Foster and H. M. Judd, *J. Chem. Soc.*, 1910, **97**, 262.

*Paper* 7/03023A
*Received* 2nd *May* 1997
*Accepted* 3rd *June* 1997