# A Convenient Synthesis of Novel Pyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazinones from Imidazo[1,2-*a*]pyridines



Héctor Salgado Zamora,* Benito Rizo, Elena Campos,
Rogelio Jiménez and Alicia Reyes

Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, IPN. México 11340 D.F. México

Received March 3, 2003

The imidazo[1,2-*a*]pyridine system was investigated as a synthon for the building of very attractive fused triazines, a planar, angular *tri*-heterocycle with potential biological activity. Thus ethyl 3-nitroimidazo[1,2-*a*]pyridine-2-carboxylate was treated with ammonia or with an excess of primary amines to generate the corresponding substituted nitro carboxamidoimidazopyridines. The nitro substituent in the latter products, was reduced to yield 3-amino-2-carboxamidoimidazo[1,2-*a*]pyridine derivatives, which in turn were treated with nitrous acid to furnish 1-oxo-2-substituted pyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazines.

*J. Heterocyclic Chem.*, **41**, 91 (2004).

Imidazo[1,2-*a*]azines properly bifunctionalized are important synthons for the building of fused *tri* or *tetra*-heterocycles [1], which display interesting biological activities [2]. Imidazo[1,2-*a*]pyridines on their own have been investigated in relation to diverse pharmacological activities [3]. On the other hand derivatives of benzofused triazines have been evaluated as potential agents for the treatment of anxiety and depressive states [4]. 1,2,3-Triazines condensed to the pyrazole and imidazole nucleus have attracted considerable attention due to its potential biological activity. [5]

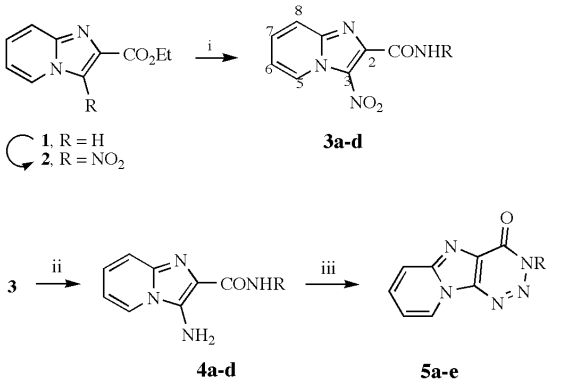
We were interested in preparing triazinones fused to the imidazopyridine nucleus and evaluate their potential affinity of binding to dopaminergic and adrenergic receptors. The planar fixed geometry of these heterocycles makes them attractive candidates for screening in relation to other biological activities.

A fine research on the formation of triazines from anthranylate esters is available [6]. We then sought for an appropriately 2,3-substituted imidazo[1,2-*a*]pyridine and found compound **1** a suitable candidate. In this study, we present the results of the investigation carried out on the imidazopyridine nucleus as a synthon for the construction of a rigid geometry *tri*-heterocycle system containing a 1,2,3-triazine ring.

The synthetic approach shown in scheme 1 was followed. Accordingly, the readily available ethyl imidazo[1,2-*a*]pyridine-2-carboxylate **1**, [7] was easily nitrated at low temperature with concentrated nitric acid in sulfuric acid. The ease of electrophilic substitution at position 3- in these systems allowed the formation of 3-nitro imidazo[1,2-*a*]pyridine-2-carboxylate **2** in good yield (80 %).

Formation of the amide was preferred over preparation of the corresponding anthranylate ester, which would have been less reactive towards ammonia. Thus, nitro ester **2** was treated with ammonium hydroxide saturated with ammonia at room temperature and from the heterogeneous mixture, the corresponding amide **3a** was isolated in good yield. Other primary amines were heated with compound **2** in the absence of solvent (an excess of the amine was required) to yield the corresponding crude 3-nitro-2-carboxamido imidazo[1,2-*a*]pyridines **3**. These products were recrystallized either from water or ethyl alcohol. In order to improve the reaction time (4-5 h) of the latter process, experiments were carried out using an alternative source of energy such as IR radiation [8]. Indeed the reaction time dropped dramatically under these conditions, a maximum of 40 min were required to complete the reaction. In spite of this result, conventional heating was preferred since it allowed the use of larger quantities of reactants.

Scheme 1




i, $RNH_2$/heat; ii, $Na_2S_2O_4$/THF/$H_2O$/60- 70 °C; iii, $NaNO_2$/HCl/$H_2O$/0-5 °C
R; a = H, b = $PhCH_2$, c = $Ph(CH_3)CH$, d = Cyclohexyl, e = Et

The nitrocarboxamido substituted imidazo[1,2-*a*]pyridines **3** were fully characterized through conventional spectroscopic methods. The numbering of the structures in Scheme 1 was based on early reports dealing with $^1H$ nmr assignments [9] on these systems. The nitroamides **3** were then reduced to the corresponding 3-amino-2-carboxamido imidazo[1,2-*a*]pyridines **4** with sodium dithionite in a mixture THF/$H_2O$, in preference to other reducing agents such as ethanolic or aqueous stannous chloride or zinc, which turned out to be low yielding processes. Compounds **4** were separated from the reaction mixture

and further purified by percolation through a short column of silica gel and fully characterized.

Finally a diazotation reaction was performed on compounds **4** using 2 equivalents of sodium nitrite in dilute hydrochloric acid. Adjusting the pH of the reaction mixture to 7, using sodium bicarbonate precipitated the fused triazinones. The crude products were separated, further purified by recrystallization and characterized. Compound **5e** was prepared in good yield by a condensation reaction of **5a** with ethyl bromide in DMF containing $K_2CO_3$.

A salient feature in the $^1$H NMR spectra of products **3**, **4** and **5** is the influence (through bonding) on the H–5 chemical shift exerted by the substituent at the heterocycle 3-position. Thus in products **3** (3-nitro substituted), H-5 showed in the range δ 9.27–9.37, then in products **4** (3-amino substituted) the chemical shift appeared upfield at δ 8.08–8.53. The signal for H-5 is shifted downfield in products **5** (δ 9.03 for **5a** in DMSO) thus reflecting the electron withdrawing character of the triazino substituent.

Currently the synthesis of other fused heterocycles to the imidazo[1,2-*a*]pyridine nucleus are under investigation

## EXPERIMENTAL

Melting points were measured on an Electrothermal melting point apparatus and are uncorrected. $^1$H and $^{13}$C nmr spectral data were recorded at 300 and 75 MHz respectively using a Bruker DPX 300 MHz NMR spectrometer. Chemical shifts (δ) are given in parts per million downfield from TMS ($\delta_H = 0$). Mass spectra were obtained with a Jeol JMSAX505HA instrument. Column chromatography was carried out with silica gel (Merck 60, 70-230 mesh) as the adsorbent.

2-Carbamoyl-3-nitroimidazo[1,2-*a*]pyridine (**3a**).

To a stirred suspension of ethyl 3-nitroimidazo[1,2-*a*]pyridin-2-carboxylate (1.0 g, 2.1 mmol) in water (10 mL), a solution of ammonium hydroxide (15 mL) was added at room temperature. A stream of ammonia gas was passed during two hours. After 4 h, the heterogeneous reaction mixture was filtered, the solid collected by filtration and washed with cold water (2 x 5 mL) and cold ethanol (5 mL). Further recrystallization from water afforded (**3a**) as colorless needles, 88 % yield, mp 275-276 °C. $^1$H nmr (DMSO-$d_6$): δ 9.27 (d, J = 6.9 Hz, 1H, H-5); 8.07 (bs, 1H, N*H*); 7.92 (m, 2H, H-8 and N*H*); 7.80 (dd, J = 9.0, 7.2 Hz,1H, H-7); 7.47 (dd, J = 7.2, 6.9 Hz, 1H, H-6); $^{13}$C nmr: δ 155.61, 147.11, 139.56, 132.91, 129.31, 126.07, 118.52, 115.38; ms: m/z (%) 206 $M^+$(13.6).

*Anal.* Calcd. for $C_8H_6N_4O_3$: C, 46.60; H, 2.96; N, 27.18. Found: C, 46.42; H, 3.05; N, 27.93.

3-Nitro-2-carboxamidoimidazo[1,2-*a*]pyridine (**3b-d**).

General procedure.

Ethyl 3-nitroimidazo[1,2-*a*]pyridin-2-carboxylate (0.5 g, 2.1 mmol) was heated with the corresponding primary amine (4.6 mmol) during 4-5 h. The reaction mixture was then allowed to cool to room temperature whereupon a solid formed, this was collected by filtration and washed with cold ethanol. Further recrystallization from water or ethanol afforded the desired amide.

2-*N*-Benzylcarboxamido-3-nitroimidazo[1,2-*a*]pyridine (**3b**).

This compound was obtained in 85 % yield, mp 187–189 °C, following the general procedure; $^1$H nmr (DMSO-$d_6$): δ 9.31 (d, J=6.6 Hz, 1H, H-5); 9.20 (bs, 1H, N*H*); 7.96 (d, J=8.7 Hz, 1H, H-8); 7.83 (dd, J=8.7, 7.2 Hz, 1H, H-7); 7.50-7.20 (m, 6H, H-6 and -$C_6H_5$); 4.50 (d, J=5.1 Hz, 2H, $CH_2$); $^{13}$C nmr; δ 159.50, 144.00, 131.06, 127.49, 118.93, 117.58, 48:74, 32.67, 25.44, 24.65; ms: m/z (%) 297 ( M +H)$^+$ (3).

*Anal.* Calcd. for $C_{15}H_{12}N_4O_3$: C, 60.81; H, 4.05; N, 18.92. Found: C, 60.66; H, 4.00; N, 18.70.

2-*N*-(*R*)-Phenylethylcarboxamido-3-nitroimidazo[1,2-*a*]pyridine (**3c**).

This compound was obtained in 96% yield, mp 176–177 °C following the general procedure. $^1$H nmr (DMSO-$d_6$): δ 9.37 (d, J=6.9 Hz, 1H, H-5); 9.01 (d, J=7.5 Hz, 1H, N*H*); 7.87 (d, J=8.7 Hz, 1H,H-8); 7.77 (dd, J=8.7, 7.2 Hz,1H, H-7); 7.37 (m, 6H, H-6 and –$C_6H_5$);5.26 (m, 1H, C*H*); 1.57 (d, J=7.5 Hz, 3H, $CH_3$).$^{13}$C nmr: δ 161.40, 145.00, 144.86, 143.86, 131.90, 129.01, 128.73, 128.03, 127.97, 127.35, 126.71, 126.30, 118.87, 118.14, 49.09, 22.34; ms: m/z (%) 311 ( M+H)$^+$ ( 4).

*Anal.* Calcd. for $C_{16}H_{14}N_4O_3$: C, 61.93; H, 4.52; N, 18.06. Found: C, 61.78; H, 4.83; N, 18.12.

2-*N*-Cyclohexylcarboxamido-3-nitroimidazo[1,2-*a*]pyridine (**3d**).

This compound was obtained in 88% yield, mp 205–206 °C following the general procedure. $^1$H nmr (deuteriochloroform): δ 9.32 (d, J=6.9 Hz, 1H, H-5); 7:82 (d, J=9.0 Hz, 1H, H-8); 7.70 (dd, J=9.0, 7.2 Hz, 1H, H-7); 7.33 (dd, J=7.2, 6.9 Hz,1H, H-6); 7.13 (bs; 1H, N*H*); 4.10 (m, 1H, $CH_{cyclohexyl}$); 2.13-1.20 (m, 10H, $CH_{2cyclohexyl}$); $^{13}$C nmr: δ 162.51, 145.16, 144.99, 139.28, 132.74, 129.09, 128.67, 128.00, 127.66, 118.91, 118.59, 42.97; ms: m/z (%) 289 (M+H)$^+$ (5).

*Anal.* Calcd. for $C_{14}H_{16}N_4O_3$: C, 58.33; H, 5.57; N, 19.44. Found: C, 58.51; H, 5.40; N, 19.93.

3-Amino-2-carboxamidoimidazo[1,2-*a*]pyridines (**4a-d**).

General Procedure.

3-Nitro-2-carboxamidoimidazo[1,2-*a*]pyridine (**3**) (3 g, 14.5 mmol) was dissolved in a mixture THF/$H_2O$ v/v (20/10), sodium dithionite (2.53 g, 14.4 mmol) was added and heating started, until a gentle reflux was reached. Then every half an hour for two hours, a half equivalent of sodium dithionite was added. The reaction end was marked when no change in coloration after sodium dithionite addition was observed. The reaction was then allowed to cool to room temperature and extracted (EtOAc). Extracts were combined, dried (anh. $Na_2SO_4$), and solvent removed under vacuum. The residue was further purified by recrystallization or by filtration through a short column of silica gel.

3-Amino-2-carboxamidoimidazo[1,2-*a*]pyridine (**4a**).

This compound was obtained in 52% yield, mp 237–239 °C following the general procedure; $^1$H nmr (DMSO-$d_6$): δ 8.08 (d, J=6.0 Hz, 1H, H-5); 7.30 (d, J=8.7 Hz, 1H, H-8); 7.29 (bs, 1H, N*H*); 7.09 (bs, 1H, N*H*); 7.02 (dd, J= 8.7, 6.6 Hz, 1H, H-7);

6.77 ( dd, J=6.6, 6.0 Hz, 1H, H-6); 6.11 (bs, 2H, N$H_2$); ms: m/z (%) 176, $M^+$ (100).

*Anal*. Calcd. for $C_8H_8N_4O$: C, 54.54; H, 4.50; N, 31.81. Found: C, 54.40; H, 4.87; N, 31.69.

3-Amino-2-*N*-benzylcarboxamidoimidazo[1,2-*a*]pyridine (**4b**).

This compound was obtained in 80% yield, mp 139-140 °C following the general procedure; $^1$H nmr (DMSO-$d_6$,): δ 8.53 (t, J=6.3Hz, 1H, N*H*); 8.13 (d, J=6.9 Hz, 1H, H-5); 7.25 (m, 6H, H-8 and –$C_6H_5$); 7.06 ( dd, J=9.0, 6.6 Hz, 1H, H-8); 6.80 (dd, J=6.9, 6.6 Hz, 1H, H-6); 6.14 (bs, 2H, N$H_2$); 4.44 (d, J=6.3 Hz, 2H, C$H_2$); $^{13}$C nmr: δ 165.13, 140.73, 137.30, 135.67, 128.64, 127.80, 127.05, 123.88, 123.54, 117.84, 116.50, 111.87, 42.12; ms: m/z (%) 266, $M^+$ (100).

*Anal*. Calcd. for $C_{15}H_{14}N_4O$: C, 67.69; H, 5.26; N, 21.05. Found: C, 67.58; H, 5.40; N, 21.10.

3-Amino-2-*N*-(*R*)-phenylethylcarboxamidoimidazo[1,2-*a*]pyridine (**4c**).

This compound was obtained in 73% yield, mp 123-124 °C following the general procedure; $^1$H nmr (DMSO-$d_6$): δ 7.83 (d, J = 6.6 Hz, 1H, H-5); 7.78 (d, J = 7.2 Hz, 1H, N*H*); 7.10-6.80 (m, 6H, H-8 and –$C_6H_5$); 6.71 (dd, J = 9.0, 6.9 Hz,1H, H-7); 6.45 (dd, J = 6.9, 6.6 Hz, 1H, H-6); 5.72 (s, 2H, N$H_2$); 4.79 (m, 1H, CH); 1.13 (d, J = 7.2, 3H, $CH_3$); $^{13}$C nmr: δ 163.90, 145.14, 136.81, 135.28, 128.22, 126.59, 126.21, 123.34, 123.05, 117.44, 116.06, 111.37, 47.49, 22.26; ms: m/z (%) 280 $M^+$, (96).

*Anal*. Calcd. for $C_{16}H_{16}N_4O$: C, 68.57; H, 5.71; N, 20.00. Found: C, 68.49; H, 5.83; N,19.57.

3-Amino-2-*N*-cyclohexylcarboxamidoimidazo[1,2-*a*]pyridine (**4d**).

This compound was obtained in 67% yield, mp 174-175 °C following the general procedure; $^1$H nmr (deuteriochloroform): δ 7.80 (dd, J= 6.9, 0.9 Hz, 1H, H-5); 7.41 (d, J=9 Hz,1H, H-8); 7.09 (ddd, J=9.0, 6.6, 0.9 Hz, 1H, H-7); 7.09 (bs, 1H,N*H*); 6.77 (dd, J=6.9, 6.6 Hz, 1H, H-6); 5.17 (bs, 2H, N$H_2$); 3.93(m, 1H, $CH_{cyclohexyl}$); 2.03-1.13 (m, 10H, $CH_{2cyclohexyl}$); $^{13}$C nmr: δ 163.98, 138.17, 133.45, 124.16, 121.65, 118.70, 117.77, 112.23, 47.78, 33.27, 25.48, 24.97, ms: m/z (%) 258, $M^+$ (100)

*Anal*. Calcd. for $C_{14}H_{18}N_4O$: C, 65.11; H, 7.02; N, 21.70. Found: C, 64.88; H, 7.01; N, 21.35.

1-Oxo-2-substitutedpyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazines (**5a-e**).

General Procedure.

The corresponding 3-Amino-2-carboxamidoimidazo[1,2-*a*]pyridines (**4**) (1.7 mmol) was dissolved in 5 *N* HCl (7 mL) and the solution cooled to 0–5 °C. Sodium nitrite (3.4 mmol) dissolved in water (5 mL) was slowly added, the reaction mixture was vigorously stirred for 15 – 20 min. Then a solution of 5% aqueous sodium bicarbonate was added until pH 7 was reached, whereupon a solid precipitated. The solid formed was collected by filtration washed with cold water and further recrystalized from ethanol.

1-Oxopyrido(1',2':1, 2)imidazo[5,4-*d*]-1,2,3-triazine (**5a**).

This compound was obtained in 54% yield, mp 207-209 °C following the general procedure; $^1$H nmr (DMSO-$d_6$): δ 9.03 (d, J= 6.9 Hz, 1H, H-5); 7.89 (d, J=9.6 Hz,1H, H-8); 7.77 (dd, J=9.6, 6.6 Hz, 1H, H-7); 7.31 (dd, J=6.9,6.6 Hz, 1H, H-6); 3.33 (bs, 1H, N*H*); $^{13}$C nmr: δ 151.61, 147.11, 139.55, 132.91, 129.30, 126.07, 118.52, 15.38; ms: m/z (%) 187 ( M)$^+$ ( 40).

*Anal*. Calcd. for $C_8H_5N_5O$: C, 51..33; H, 2.67; N, 37.43. Found: C, 51.50; H, 2.81; N, 37.29.

1-Oxo-2-benzylpyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazine (**5b**).

This compound was obtained in 69% yield, mp 250-252 °C following the general procedure; $^1$H nmr (deuteriochloroform): δ 8.82 (d, J=6.6 Hz, 1H, H-5); 7.84 (d, J=9.0 Hz, 1H, H-8); 7.65 (dd, 9.0, 7.2 Hz, 1H, H-7); 7.53 (d, J=6.6 Hz, 2H, $H_m$); 7.3 (m, 3H, $H_o$ and $H_p$); 7.20 ( dd, J=7.2, 6.6 Hz, 1H, H-6); 5.75 (s, 2H, C$H_2$); $^{13}$C nmr: δ 154.64, 147.9, 135.80, 133.14, 131.92, 129.48, 128.90, 128.65, 128.18, 124.82, 119.31, 114.92, 53.33; ms: m/z (%) 277 (M)$^+$(39).

*Anal*. Calcd. for $C_{15}H_{11}N_5O$: C, 64.98; H, 3.97; N, 25.27. Found: C,64.88; H, 4.16; N, 25.16.

1-Oxo-2-(*R*)-phenylethylpyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazine (**5c**).

This compound was obtained in 78% yield, mp 204-206 °C following the general procedure; $^1$H nmr (deuteriochloroform); δ 8.80 (d, J=6.9 Hz, 1H, H-5); 7.83 (d, J=9 Hz, 1H, H-8); 7.63 (dd, J=9.0, 6.9 Hz, 1H, H-7);7.54 (d, J=8.1 Hz, 2H, $H_m$); 7.30 (m, 3H, $H_o$ and $H_p$); 7.18 (dd, J=6.9, 6.9 Hz, 1H, H-6); 6.69 (m, 1H, C*H*); 2.07 (d, J=7.2 Hz, 3H, C$H_3$); $^{13}$C nmr: δ 154.55, 147.74, 140.42, 138.55, 131.78, 128.82, 128.48, 127.91, 127.49, 124.67, 119.17, 114.78, 55.83, 20.54; ms: m/z (%)291 ( M)$^+$ (13)

*Anal*. Calcd. for $C_{16}H_{13}N_5O$: C, 65.97; H, 4.46; N, 24.05. Found: C, 65.63; H, 4.68; N, 23.84.

1-Oxo-2-cyclohexylpyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazine (**5d**).

This compound was obtained in 66% yield, mp 225-227 °C following the general procedure; $^1$H nmr (deuteriochloroform): δ 8.82 (d, J=6.9 Hz, 1H, H-5); 7.83 (d, J=9 Hz, 1H, H-8); 7.63 (dd; J=9.0, 6.6 Hz, 1H, H-7); 7.20 (dd, J=6.6. 6.6 Hz, 1H, H-6); 5.23 (m, 1H, $CH_{cyclohexyl}$); 2.02-1.02 (m, 10H, $CH_{2cyclohexyl}$); $^{13}$C nmr: δ 154.54, 147.74, 131.71, 128.70, 125.96, 124.75, 119.25, 114.67, 56.82, 32.46, 25.75, 25.26; ms: m/z (%) 277 ( M)$^+$(39).

*Anal*. Calcd. for $C_{14}H_{15}N_5O$: C, 62.45; H, 5.57; N, 26.02. Found: C, 62.12; H, 5.71; N, 25.73.

1-Oxo-2-ethylpyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazine (**5e**).

To a suspension of $K_2CO_3$ (142 mg, 1.07 mmol) in anhydrous DMF (1 mL), and under nitrogen atmosphere, 2 *H*-1-oxo-pyrido(1',2':1,2)imidazo[5,4-*d*]-1,2,3-triazine (**5a**) (100 mg, 0.54 mmol) suspended in DMF (1.5 mL) was added. The reaction mixture was stirred for 30 min at room temperature and then bromoethane (115 mg, 1.07 mmol) was added. The reaction mixture was heated at 70 °C for 12 h and then allowed to cool to room temperature, water (15 mL) was added and extracted with ethyl acetate (3 x 15 mL). Solvent was dried (anh. $Na_2SO_4$.) removed under vacuum to leave a solid which was further recrystallized to yield (**5e**) as light brown crystals, 62 % yield, mp 229- 230 °C; $^1$H nmr (deuteriochloroform): δ 8.85 (d, J = 6.9 Hz, 1H, H-5); 7.89 (d, J = 9 Hz, 1H, H-8); 7.69 (dd, J = 9.0, 7.2 Hz, 1H, H-7); 7.22 (dd, J = 7.2, 6.9 Hz, 1H, H-6); 4.67 (q, J = 7.2 Hz, 2H, $CH_2$); 1.54 (t, J = 7.2 Hz, 3H, $CH_3$); $^{13}$C nmr δ 154.55, 147.88, 139.00, 131.85, 129.15, 124.85, 119.33, 114.81, 45.63; ms: m/z (%) 215, $M^+$ (100).

*Anal*. Calcd. for $C_{10}H_9N_5O$: C, 55.81; H, 4.18; N, 32.55. Found: C, 55.69; H, 4.36; N, 32.43.

## REFERENCES AND NOTES

[1] O. Chavignon, J. C. Teulade, M. Madesclaire, A. Gueiffier, Y. Blache, H. Viols, J. P. Chapat and G, Dauphin, *J. Heterocyclic Chem*., **29**, 691 (1992).

[2] G. J. Boryski, B. Golankiiewicz and E. DeClercq, *J. Med. Chem*., **31**, 1951 (1988).

[3] See for example: J. J. Kaminski, J. A. Bristoñ, Ch. Puchalski, R. G. Lovey, A. J. Elliot, H. Guzik, D. M. Solomon, D. J. Conn, M. S. Donalski, S-C. Wong, E. H. Gold, J. F. Long, P. J. S., Chiu, M. Steinberg and A. T. McPhail*, J. Med. Chem*., **28**, 876 (1985); S. Laneri and E. Abignente, *J. Heterocyclic Chem*., **37**, 1265 (2000).

[4] G. Caliendo, F. Fiorino, E. Perissutti, B. Severino, S. Gessi, E. Cattabriga, P. A. Borea and V. Santagada, *Eur. J. Med. Chem*., **36**, 873 (2001).

[5] M. T. Migawa and L. B. Townsend, *J. Org. Chem*., **66**, 4776 (2001).

[6] R. J. LeBlanc and K. Vaughan, *Can. J. Chem*. **50**, 2544 (1972).

[7] J. G. Lombardino, *J. Org. Chem*., **30**, 2403, (1965).

[8] G. C. Pool, J. H. Teuben, IRT Radiation as a heat source in vacuum sublimation, in Practical Organometallic Chemistry, A. L. Wayda, M. Y. Darensbourg, Eds., Symposium Series 357, Washington, D.C, 1987**,** pp 30-33**.**

[9] J. P. Paolini and R. K. Robins, *J. Heterocyclic Chem*., **2**, 53 (1965); J-C-Teulade, R. Escale, G. Grassy, J-P. Girard and J-P. Chapat, *Bull. Soc. Chim. Fr*. Part II, 529 (1979).