J. Braz. Chem. Soc., Vol. 17, No. 2, 408-411, 2006.
Printed in Brazil - ©2006 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Short Report

Microwave-Assisted Synthesis of Novel 5-Trichloromethyl-4,5-dihydro-1*H*-1-pyrazole Methyl Esters under Solvent Free Conditions

Marcos A. P. Martins,* Paulo Beck, Pablo Machado, Sergio Brondani, Sidnei Moura, Nilo Zanatta, Helio G. Bonacorso and Alex F. C. Flores

Núcleo de Química de Heterociclos (NUQUIMHE), Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria-RS, Brazil

A preparação, com bons rendimentos (70–98%), de doze novos ésteres etílicos de 5-triclorometil-4,5-diidro-1*H*-1-pirazóis, usando-se ambientalmente boas técnicas induzidas por microondas, é descrita. Estes compostos foram sintetizados a partir da reação de ciclocondensação de 1,1,1-tricloro-4-alcoxi-3-alquen-2-onas [$CCl_3C(O)C(R^2)=C(R^1)OR$, onde R, R^2 = H, alquila; R^1 = H, alquila e arila] com metil carboxilato hidrazina. As vantagens obtidas pelo uso de irradiações de microondas na ausência de solventes, em relação ao método convencional foram demonstradas.

Twelve novel 5-trichloromethyl-4,5-dihydro-1*H*-1-pyrazole ethyl esters have been synthesized in good yields (70–98%) by using environmentally benign microwave induced techniques. The compounds were synthesized from the cyclocondensation of 1,1,1-trichloro-4-alkoxy-3-alken-2-ones [$CCl_3C(O)C(R^2)=C(R^1)OR$, where R, R^2 = H, alkyl; R^1 = H, alkyl and aryl] with hydrazine methyl carboxylate. The advantages obtained by the using of microwave irradiation under solvent-free conditions, rather than a conventional method, were demonstrated.

Keywords: pyrazoles, enones, microwave irradiations, green chemistry

Introduction

Trihalomethyl substituted pyrazoles belong to an important class of compounds, which possess a wide variety of pharmaceutical and agrochemical properties.[1,2] The main synthetic method used to prepare trihalomethylpyrazoles involves a [3+2] cyclization such as the classical 1,3-diketone with hydrazines.[3] In recent years, we have developed a general synthesis of 1,1,1-trihalo-4-alkoxy-3-alken-2-ones,[4,5] important halogen-containing building blocks and their use in heterocyclic preparations (e.g. isoxazoles, pyrazoles, pyrazolium chlorides, pyrrolidines, pyrimidines, thiazines, diazepines, thiazoles, selenazoles, and quinolines) has been extensively described.[5] In particular, trichloromethyl substituted azoles are important as synthons and reagents in organic synthesis. These compounds have also been used as precursors for the synthesis of carbonyl-azole derivatives[6] in a one-pot procedure. Moreover, the pharmaceutical properties of trichloromethyl substituted pyrazolines have been reported by our research group.[7] Recently, we reported the application of microwave irradiation for the synthesis of halomethyl-substituted azoles.[8] The beneficial effects of microwave irradiation are playing an increasing role in process chemistry, especially in cases where classical methods require forcing conditions or prolonged reaction times. When processes involve sensitive reagents, or there is the possibility of compound decomposition under prolonged reactions conditions, microwaves have also shown an advantage. The use of focused microwave irradiation to decrease reaction times and improve yields has been demonstrated.[9] Microwave irradiation (MW), using commercial domestic ovens, has been recently used to accelerate organic reactions, due to its high heating efficiency, giving remarkable rate enhancement and dramatic reduction in reaction times. In recents papers were reported the application of microwave irradiation with great results for the synthesis of heterocycles, an eco-friendly methodology to prepare indazoles, pyrazolopyridines, bipyrazoles, aziridines, benzimidazoles and 2-oxazolines in solvent free conditions.[10,11] Thus, the aim of this work is to demonstrate the advantages obtained by the use of microwave irradiation for the synthesis of novel 5-trichloromethyl-4,5-dihydro-1*H*-1-pyrazole methyl esters

* e-mail: mmartins@base.ufsm.br

2 by the reaction of 1,1,1-trichloro-4-alkoxy-3-alken-2-ones **1** with methyl hydrazino carboxylate under solvent free conditions and in good yields (Scheme 1).

The 1,1,1-trichloro-4-alkoxy-3-alken-2-ones **1a–l** were synthesized from the reaction of the respective enol ether or acetal with trichloroacethyl chloride.[4]

Treatment of 1,1,1-trichloro-4-alkoxy-3-alken-2-ones **1** with methyl hydrazine carboxylate for six minutes, using microwaves (45 W) at 50–55 °C, produced the 5-trichloromethyl-4,5-dihydro-*1H*-1-pyrazole methyl esters **2**, under solvent free conditions. Conventional heating gave only moderate yields of the expected products, whereas with the use of microwave irradiation under solvent free conditions, the cyclocondensation products were obtained with a drastic reduction in reaction times (Table 1).

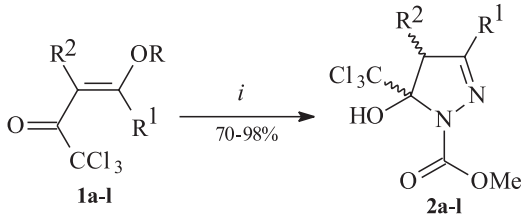
Experimental

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial supplies without further purifications. The melting points were taken on a melting point microscope Reichert–Thermovar and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) in 5 mm sample tubes at 298 K (digital resolution ±0.01 ppm) in $CDCl_3$/TMS solutions. Mass spectra were registered in a HP 6890 GC connected to a HP 5973 MSD and interfaced by a Pentium PC. The GC was equipped with a split-splitless injector, autosampler, cross-linked HP-5 capillary column (30 m, 0.32 mm of internal diameter), and helium was used as the carrier gas.

Microwave irradiations were conducted in a Panasonic M720 at a frequency of 2450 MHz, with an average energy in the sample of 45 W and the temperature measured after the completion of the reaction in the range of 50–55 °C. The measure of average energy in the sample is in agreement with methodology presented in reference 9.

*Synthesis of 5-trichloromethyl-4,5-dihydro-1H-1-pyrazole ethyl esters **2a–l** (microwave method)*

A mixture of 1,1,1-trichloro-4-alkoxy-3-alken-2-ones **1** (2 mmol) and methyl hydrazino carboxylate (2.5 mmol) was stirred for a few minutes, and then the mixture was irradiated in a microwave oven at 45 W for 6 min, at 50–55 °C (temperature after the completion of the reaction). A10% HCl solution (30 mL) was added to the reaction mixture, and the product **2** was extracted with chloroform (2 × 20 mL), washed with distilled water (2 × 30 mL) and dried with $MgSO_4$. The solvent was removed in a rotaevaporator, and the product was obtained in high purity. When necessary the product was recrystallized from cyclohexane.



[i] Reaction Conditions: $NH_2NHC(O)OMe$, 45W, 50-55 °C, 6 min.

1, 2	a	b	c	d	e	f	g	h	i	j	k	l
R^1	H	Me	Et	^{n}Pr	^{i}Pr	^{cyclo}Pr	^{n}Bu	^{i}Bu	^{t}Bu	H	Ph	4-O_2N-C_6H_4
R^2	H	H	H	H	H	H	H	H	H	Me	H	H
R	Et	Me	Me	Me	Me	Me	Me	Me	Me	Et	Me	Me

Scheme 1.

Table 1. Yields[a] and reaction conditions[b] used for the microwave assisted synthesis of **2**

Product	Microwave method [b] Reaction time (min)	Yield (%)	Conventional method Reaction time (h)	Yield(%)	Product	Microwave method [b] Reaction time (min)	Yield (%)	Conventional method Reaction time (h)	Yield (%)
2a	6	71	24	70	**2g**	6	86	24	79
2b	6	70	24	72	**2h**	6	89	24	70
2c	6	98	24	78	**2i**	6	87	24	75
2d	6	92	24	75	**2j**	6	80	24	73
2e	6	76	24	70	**2k**	6	75	24	74
2f	6	93	24	78	**2l**	6	70	24	70

[a] Yields of isolated products; [b] reaction conditions: solvent free, MW, 45 W, 50–55°C.

Synthesis of 5-trichloromethyl-4,5-dihydro-1H-1-pyrazole ethyl esters ***2a–l*** *(conventional method)*

A solution of **1** (2 mmol) and NH_2NHCO_2Me (2.5 mmol) in methanol (30 mL) was stirred under reflux for 24 hours. Water was added (60 mL) and the organic phase was extracted with $CHCl_3$ (2 × 20 mL). The organic extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The work-up was carried out as described for the *microwave method*.

2a. $C_6H_7Cl_3N_2O_3$, mw 261.48, oil. ^{1}H NMR δ (*J*, Hz) 7.10 (s, 1H, H-3), 3.28 (d, 1H, *J* 19, H-4a), 3.71 (d, 1H, *J* 19, H-4b), 3.90 (s, 3H, OMe). ^{13}C NMR δ 154.82 (C=O), 146.6 (C-3), 103.2 (C-5), 98.8 (CCl_3), 53.6 (OMe), 47.2 (C-4). Anal. Calc.: C, 27.56%; H, 2.70%; N, 10.71%. Found: C, 27.43%; H, 2.69%; N, 10.66%. MS *m/z*, (%) 143 (M^+ - CCl_3, 100); 111 (52), 59 (CO_2Me, 26).

2b. $C_7H_9Cl_3N_2O_3$, mw 275.51, mp 101 – 103 °C. ^{1}H NMR δ (*J*, Hz) 3.29 (d, 1H, *J* 19, H-4a) 3.57 (d, 1H, *J* 19, H-4b), 2.09 (s, 3H, Me), 3.89 (s, 3H, OMe). ^{13}C NMR *d* 156.7 (C-3), 154.0 (C=O), 111.1 (C-5), 101.9 (CCl_3), 53.4 (OMe), 47.9 (C-4), 15.5 (Me). Anal. Calc.: C, 30.52%; H, 3.29%; N, 10.17%. Found: C, 30.48%; H, 3.28%; N, 10.15%. MS *m/z*, (%) 157 (M^+ - CCl_3, 99) 125 (100), 83 (38).

2c. $C_8H_{11}Cl_3N_2O_3$, mw 289.53, mp 76 – 78 °C. ^{1}H NMR δ (*J*, Hz) 3.71 (d, 1H, *J* 19, H-4a), 3.24 (d, 1H, *J* 19, H-4b) 3.90 (s, 3H, OMe), 3.26 (q, 2H, CH_2), 2.01 (t, 3H, CH_3). ^{13}C NMR δ 161.7 (C-3), 154.7 (C=O), 111.7 (C-5), 102.7 (CCl_3), 53.3 (OMe), 47.1 (C-4) 23.0 (CH_2) 10.0 (CH_3). Anal. Calc.: C, 33.19%; H, 3.83%; N, 9.67%. Found: C, 33.20%; H, 3.80%, N, 9.66%. MS *m/z*, (%) 171 (M^+ - CCl_3, 100), 139 (81), 111 (47).

2d. $C_9H_{13}Cl_3N_2O_3$, mw 303.56, mp 59 – 61 °C. ^{1}H NMR δ (*J*, Hz) 3.71 (d, 1H, *J* 19, H-4a), 3.24 (d, 1H, *J* 19, H-4b) 3.81 (s, 3H, OMe) 2.29 (t, 2H, CH_2), 1.57 (m, 2H, CH_2), 0.91 (t, 3H, CH_3). ^{13}C NMR δ 164.7 (C-3), 160.0 (C=O), 108.0 (C-5), 105.0 (CCl_3) 53.4 (OMe), 53.0 (C-4) 36.8, 24.7 ($2CH_2$) 18.7 (CH_3). Anal. Calc.: C, 35.61%; H, 4.32%; N, 9.23%. Found: C, 35.37%; H, 4.29%, N, 9.17%. MS *m/z*, (%) 185 (100), 139 (76), 111 (42).

2e. $C_9H_{13}Cl_3N_2O_3$, mw 303.56, mp 63 – 65 °C. ^{1}H NMR δ (*J*, Hz) 3.50 (d, 1H, *J* 19, H-4a), 3.28 (d, 1H, *J* 19, H-4b) 3.88 (s, 3H, OMe), 2.79 (m, 1H, CH), 1.21 (d, 3H, CH_3), 1.18 (d, 3H, CH_3). ^{13}C NMR δ 164.1 (C-3), 155.0 (C=O), 111.6 (C-5), 102.8 (CCl_3), 53.6 (OMe), 45.3 (C-4), 25.3 (CH), 22.0 ($2CH_3$). Anal. Calc.: C, 35.61%; H, 4.32%; N, 9.23%. Found: C, 35.60%; H, 4.22%, N, 9.24%. MS *m/z*, (%) 185 (M^+ - CCl_3, 100), 153 (47), 111 (71).

2f. $C_9H_{11}Cl_3N_2O_3$, mw 301.55, mp 113 – 115 °C. ^{1}H NMR δ (*J*, Hz) 3.30 (d, 1H, *J* 19, H-4a), 3.15 (d, 1H, *J* 19, H-4b) 3.88 (s, 3H, OMe), 1.30 (CH), 0.95, 0.85 (m, 4H, $2CH_2$). ^{13}C NMR δ 161.5 (C-3), 155.0 (C=O), 103.5 (C-5), 99.9 (CCl_3), 53.7 (OMe), 45.7 (C-4), 11.3 (CH), 6.68, 6.51 ($2CH_2$). Anal. Calc.: C, 35.85%; H, 3.68%; N, 9.29%. Found: C, 35.84%; H, 3.65%, N, 9.21%. MS *m/z*, (%) 183 (M^+ - CCl_3, 100) , 151 (55).

2g. $C_{10}H_{15}Cl_3N_2O_3$, mw 317.59, mp 59 – 61 °C. ^{1}H NMR δ (*J*, Hz) 3.50 (d, 1H, *J* 19, H-4a), 3.23 (d, 1H, *J* 19, H-4b) 3.86 (s, 3H, OMe), 2.38 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.36 (m, 2H, CH_2), 0.91 (t, 3H, CH_3). ^{13}C NMR δ 159.7 (C-3), 154.7 (C=O), 111.6 (C-5), 102.7 (CCl_3), 47.2 (C-4), 53.2 (OMe), 30.9, 29.6, 22.0 ($3CH_2$), 13.55 (CH_3). Anal. Calc.: C, 37.82%; H, 4.76%; N, 8.82%. Found: C, 37.57%; H, 4.73%, N, 8.76%. MS *m/z*, (%) 199 (M^+ - CCl_3, 100), 167 (32), 111 (14), 57 (73).

2h. $C_{10}H_{15}C_{13}N_2O_3$, mw 317.59, mp 57 – 59 °C. ^{1}H NMR δ (*J*, Hz) 3.55 (d, 1H, *J* 19, H-4a), 3.22 (d, 1H, *J* 19, H-4b) 3.89 (s, 3H, OMe), 2.29 (d, 2H, CH_2), 1.95 (m, 1H, CH), 1.0 (d, 6H, $2CH_3$). ^{13}C NMR δ 159.2 (C-3), 155.1 (C=O), 111.6 (C-5), 102.8 (CCl_3), 47.2 (C-4), 53.6 (OMe), 38.9 (CH_2), 26.2 (CH), 22.7, 22.3 ($2CH_3$). Anal. Calc.: C, 37.82%; H, 4.76%; N, 8.82%. Found: C, 37.49%; H, 4.72%, N, 8.73%. MS *m/z*, (%) 199 (M^+ - CCl_3, 100), 167 (24), 57 (90).

2i. $C_{10}H_{15}Cl_3N_2O_3$, mw 317.59, mp 105 – 107 °C. ^{1}H NMR δ (*J*, Hz) 3.59 (d, 1H, *J* 19, H-4a), 3.26 (d, 1H, *J* 19, H-4b), 3.87 (s, 3H, OMe), 1.23 (s, 9H, $3CH_3$). ^{13}C NMR δ 165.6 (C-3), 154.7(C=O), 103.2 (C-5), 99.7 (CCl_3), 52.9 (OMe), 44.8 (C-4), 33.6 (C-^{t}Bu), 27.0 ($3CH_3$). Anal. Calc.: C, 37.82%; H, 4.76%; N, 8.82%. Found: C, 37.45%; H, 4.71%; N, 8.72%. MS *m/z*, (%) 199 (M^+ - CCl_3, 99), 167 (14), 57(100).

2j. $C_7H_9Cl_3N_2O_3$, mw 275.51, mp 95 – 97 °C. ^{1}H NMR δ 7.0 (s, 1H, H-3), 3.90 (s, 3H, OMe), 3.64 (q, 1H, H-4a), 1.27 (d, 3H, CH_3). ^{13}C NMR δ 155.4 (C-3), 151.7 (C=O), 104.3 (C-5), 98. 7 (CCl_3), 53.8 (OMe), 50.4 (C-4) 12.1 (CH_3). Anal. Calc.: C, 30.52%; H, 3.29%; N,10.17%. Found:C, 30.24%; H, 3.26%; N, 10.07%. MS *m/z*, (%) 157 (M^+ - CCl_3 , 100), 125 (77), 97 (43).

2k. $C_{12}H_{11}Cl_3N_2O_3$, mw 337.58, mp 141 – 143 °C. ^{1}H NMR δ (*J*, Hz) 3.76 (d, 1H, *J* 19, H-4a), 3.50 (d, 1H, *J*

19, H-4b), 3.95 (s, 3H, OMe), 7.41-7.74 (m, 5H, Ph). ^{13}C NMR δ 154.0 (C-3), 153 (C=O), 131.0 – 121.0 (6C, Ph), 112.8 (C-5), 90.0 (CCl_3), 54.0 (OMe), 43.2 (C-4). Anal. Calc.: C, 42.70%; H, 3.28%; N, 8.30%. Found:C, 42.57%; H, 3.26%; N, 8.26%. MS *m/z*, (%) 219 (M^+ - CCl_3, 100), 77 (Ph, 80), 187 (30), 288 (82).

2l. $C_{12}H_{10}Cl_3N_3O_5$, mw 382.57, mp 158 – 160 °C. ^{1}H NMR δ (*J*, Hz) 4.04 (d, 1H, *J* 19, H-4a), 3.83 (d, 1H, *J* 19, H-4b), 3.96 (s, 3H, OMe), 7.91 (d, 2H, Ph), 8.29 (d, 2H, Ph). ^{13}C NMR δ 155.0 (C-3), 152.6 (C=O), 103.1 (C-5), 101.1 (CCl_3), 54.0 (OMe), 46.0 (C-4), 147.0 – 123.0 (6C, Ph). Anal. Calc.: C, 37.68%; H, 2.63%; N,10.98%. Found: C, 37.60%; H, 2.61%; N, 10.92%.MS *m/z*, (%) 263 (M+1 – CCl_3, 90), 218 (100), 59 (60).

Acknowledgments

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/PADCT) and Fundação de Amparo à pesquisa do Estado do Rio Grande do Sul (FAPERGS) for financial support. The fellowships from CNPq, CAPES and FAPERGS are also acknowledged.

References

1. Hainzl, D.; Cole, L.M.; Casida, J.E.; *Chem. Res. Toxicol.* **1998**, *11*, 1529.
2. Talley, J. J.; Bronw, D. L.; Carter, J. S.; Graneto, M. J.; Kobolt, C. M.; Mansferrer, J. L.; Perkins, W. E.; Rogers, R. S.; Shaffer, A. F.; Zhang, Y. Y.; Zweifel, B. S.; Seibert, K.; *J. Med. Chem.* **2000**, *43*, 775; *J. Med. Chem.* **1997**, *40*, 1347; Djuric, S. W.; BaMaung, N. Y.; Basha, A.; Liu, H.; Luly, J. R.; Madar, D. J.; Sciotti, R. J.; Tu, N. P.; Wagenaar, F. L.; Wiedman, P. E.; Zhou, X.; Ballaron, S.; Bauch, J.; Chen, Y.- W.; Chiou, X. G.; Fey, T.; Gauvin, D.; Gubbins, E.; Hsieh, G. C.; Marsch, K. C.; Mollison, K. W.; Pong, M.; Shaughnessy, T. K. Sheets, M. P.; Smith, M.; Trevillyan, J. M.; Warrior, U.; Wegner, C. D.; Carter, G. W.; *J. Med. Chem*. **2000**, *43*, 2975.
3. Pushkevich, K. I.; Saloutin, V. I.; Postovskii, I.; *Russ. Chem. Rev*. **1981**, *50*, 180; Lyga, J. W.; Patera, R. M.; *J. Heterocycl. Chem*. **1990**, *27*, 919; Claire, P. P. K.; Coe, P. L.; Jones, C. J.; McCleverty, J. A.; *J. Fluorine Chem*. **1991**, *51*, 283; Bumgardner, C. L.; Sloop, J. C.; *J. Fluorine Chem*. **1992**, *56*, 141; Song, L.; Chu, Q.; Zhu, S.; *J. Fluorine Chem*. **2001**, *107*, 1076; Song, L.; Chu, Q.; Zhu, S.; *J. Fluorine Chem*. **2001**, *111*, 201; Singh, S. P.; Kumar, D.; Jones, B. G.; Threadgill, M. D.; *J. Fluorine Chem*. **1999**, *94*, 199.
4. Colla, A.; Martins, M. A. P.; Clar, G.; Krimmer, S.; Fischer, P.; *Synthesis* **1991**, 483; Martins, M. A. P.; Bastos, G. P.; Bonacorso, H. G.; Zanatta, N.; Flores, A. F. C.; Siqueira, G. M.; *Tetrahedron Lett*. **1999**, *40*, 4309; Bonacorso, H. G.; Martins, M. A. P.; Bittencourt, S. R. T.; Lourega, R. V.; Zanatta, N.; Flores, A. F. C.; *J. Fluorine Chem*. **1999**, *99*, 177; Martins, M.A.P.; Emmerich, D.J.; Pereira, C.M.P.; Cunico, W.; Rossato, M.; Zanatta, N.; Bonacorso, H.G.; *Tetrahedron Lett*. **2004**, *45*, 4935.
5. Martins, M. A. P.; Cunico, W.; Pereira, C.M.P; Flores, A.F.C.; Bonacorso H.G.; Zanatta, N.; *Curr. Org. Synth.* **2004**, *1,* 391.
6. Martins, M. A. P.; Freitag, R.; Flores, A.F.C.; Zanatta, N.; *Synthesis* **1995**, 1491; Martins, M. A. P.; Flores, A.F.C.; Bastos, G. P.; Sinhorin, A.; Bonacorso, H.G.; Zanatta, N.; *Tetrahedron Lett.* **2000**, *41*, 293; Flores, A. F. C.; Zanatta, N.; Rosa, A.; Brondani, S.; Martins, M. A. P.; *Tetrahedron Lett.* **2002**, *43*, 5005; Martins, M. A. P.; Emmerich, D.; Beck, P.; Cunico, W.; Pereira, C.M.P.; Sinhorin, A.P.; Brondani, S.; Peres, R.; Teixeira, M.V.M.; Bonacorso, H.G.; Zanatta, N.; *Synth. Commun.* **2004**, *10*, 1915.
7. Souza, F. R.; Souza, V. T.; Ratzlaff, V.; Borges, L. P.; Oliveira, M. R.; Bonacorso, H. G.; Zanatta, N.; Martins, M. A. P.; Mello, C. F. *Eur. J. Pharmacol.* **2002**, *451*, 141; Godoy, M. C. M.; Fighera, M. R.; Souza, F. R.; Flores, A. E.; Rubin, M. A.; Oliveira, M. R.; Zanatta, N.; Martins, M. A. P.; Bonacorso, H. G.; Mello, C. F.; *Eur. J. Pharmacol.* **2004**, *496*, 93; Tabarelli, Z.; Rubin, M. A.; Berlese, D. B.; Sauzem, P. D.; Missio, T. P.; Teixeira, M. V.; Sinhorin, A. P.; Martins, M. A. P. ; Zanatta, N.; Bonacorso, H. G.; Mello, C. F.; *Brazilian J. Med. Biol. Res.* **2005**, *37*, 1531.
8. Martins, M. A. P.; Beck, P.; Cunico, W.; Pereira, C. M. P.; Sinhorin, A. P.; Blanco, R. F.; Peres, R.; Bonacorso, H. G.; Zanatta, N.; *Tetrahedron Lett*. **2002**, *43*, 7005; Martins, M.A.P.; Blanco, R.F.; Pereira, C.M.P; Beck, P.; Brondani, S.; Cunico, W.; Bonacorso, H.G.; Zanatta, N.; *Tetrahedron Lett.* **2003**, *44*, 6669.
9. Kingston, H. M.; Jassie, L. B.; *Introduction to Microwave Sample Preparation—Theory and Practice*, ACS: Washington, 1988; Pecoraro, E.; Davolos, M. R.; Jafelicci, M. J.; *Quim. Nova* **1997**, *20*, 89; Lidström, P.; Tierney, J.; Wathey, B.; Westman, J.; *Tetrahedron* **2001**, *57*, 9225.
10. Díaz-Ortiz, A.; la Hoz, A.; Langa, F.; *Green Chem*. **2000**, *2*, 165.
11. Varma, R. S.; *Green Chem*. **1999**, *1*, 43; Varma, R. S.; *Pure Appl. Chem.* **2001**, *1*, 193.

Received: September 21, 2005
Published on the web: February 13, 2006