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Clean and efficient microwave-solvent-free conversion of homochiral amines, α-amino alcohols and α-amino acids to their chiral 2-substituted pyrrole derivatives

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Abstract—Efficient synthesis of 1,2-disubstituted homochiral pyrroles has been achieved by a two-component coupling of chloroenones and amine compounds on the surface of silica gel without any solvent under microwave irradiation.

1. Introduction

Compounds containing a pyrrole ring can be found in many naturally occurring compounds and have been found to be useful for applications in medicine and agriculture.[1] Chiral pyrrole derivatives of amines and amino acids are important starting materials for the synthesis of many different biologically active compounds. Several useful variants of classical methods can be found in the literature.[2] A stereoselective approach to the synthesis of indolizidine alkaloids, based on the reaction of pyrrole derivatives of amino acids has been reported.[3] C-2 substituted pyrrole derivatives provide access to substituted indolizidine alkaloids (**A**), hydroxylactams (**B**) unsaturated γ-lactams (**C**) and bicyclic lactams (**D**) (Fig. 1).

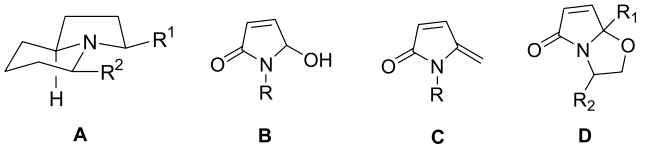

Figure 1.

The most widely used approach to pyrrole synthesis is the Paal–Knorr method in which 1,4-dicarbonyl compounds[4] and their masked equivalents such as tetrahydro-2,5-dimethoxyfuran, are converted to pyrrole derivatives with primary amines.[3] During the condensation reaction for the formation of the pyrrole ring with amino acids, partial racemization often occurs. Therefore, the development of a flexible and selective method to obtain such compounds is desirable. As we described in our previous paper,[5] we have designed a convenient new route to 2-alkyl substituted pyrrole rings from amines, amino alcohols and amino acids with chloroenones. The use of microwaves for carrying out these reactions under solvent free conditions provides advantages for the synthesis of numerous types of pyrroles. As part of our continued interest in the chemistry of substituted pyrroles, we wish to report here an efficient microwave-assisted one-pot synthesis of pyrroles by coupling chloroenones and amine compounds onto the surface of silica gel.

2. Results and discussion

Haloenones are valuable intermediates for the construction of nitrogen heterocycles. Chloroenones **2a–d** provide a four carbon unit with a carbonyl and halide functionality to form pyrrole rings with primary amines. As we previously reported, the refluxing of amine compounds with chloroenone in benzene-triethylamine and water for 4–6 h furnished the 2-substituted pyrrole derivatives in 71–95% yields (Table 1).[5] The use of microwaves for carrying out reactions in the laboratory provides advantages for the synthesis of numerous types of compounds. When the technique is applied successfully, the most evident improvements are reduced time of reaction, cleaner reactions due to fewer side-reactions, and the use of minimal quantities of solvent. Thus, microwave assisted

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Table 1. The synthesis of 2-substituted pyrroles

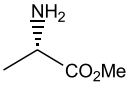
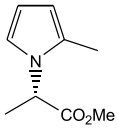
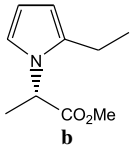
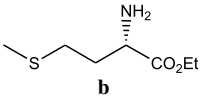
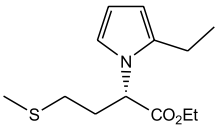
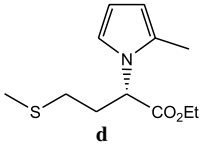
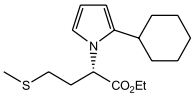
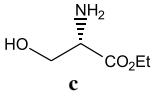
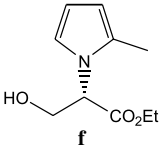
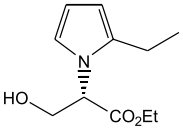
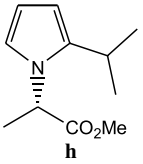
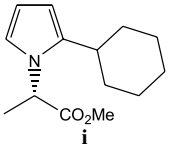
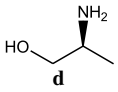
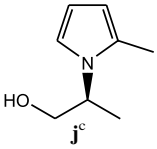
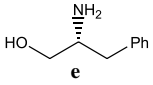
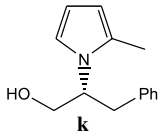
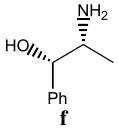
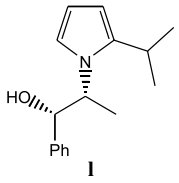
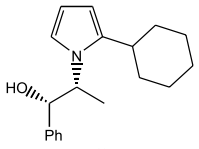
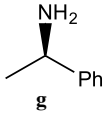
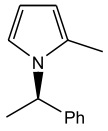
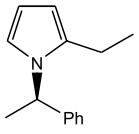
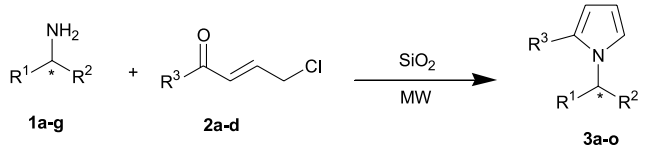
Amine **1**	Chloroenone **2** R=	Pyrrole **3**[a]	Heating method		Microwave	
			Reaction time (h)	Yield[b] (%)[ref]	Reaction time (min)	Yield[b] (%)
 **a**	CH_3 **a**	 **a**	6	80[5b,c]	5	79
a	C_2H_5 **b**	 **b**	6	74	4	68
 **b**	**b**	 **c**	5	80	6	82
b	**a**	 **d**	5	71	4	70
b	C_6H_{11} **c**	 **e**	6	73	6	74
 **c**	**a**	 **f**	6	75[5d,e]	5	83
c	**b**	 **g**	4	79	4	77
a	$(CH_3)_2CH$ **d**	 **h**	5	76[5b,c]	5	84
a	**c**	 **i**	5	72[5b,c]	5	83
 **d**	**a**	 **j**[c]	5	95[5d,e]	5	88

Table 1 (*continued*)

Amine **1**	Chloroenone **2** R=	Pyrrole **3**[a]	Heating method		Microwave	
			Reaction time (h)	Yield[b] (%)[ref]	Reaction time (min)	Yield[b] (%)
 **e**	**a**	 **k**	5	84[5d,e]	5	87
 **f**	**d**	 **l**	4	85[5b,c]	6	83
f	**c**	 **m**	4	81[5b,c]	5	87
 **g**	**a**	 **n**	6	90[5b,c]	5	88
g	**b**	 **o**	5	72	4	84

[a] The compounds **3a**,**f**,**h**,**i**,**j**,**k**,**l**,**m**,**n** are known and have been identified by comparison of spectral data with those reported in the literature.
[b] Isolated yields.
[c] $[\alpha]_D^{20}=9.9$ (*c* 1.2, $CHCl_3$); lit.[5d] $[\alpha]_D^{20}=-9.6$ (*c* 1.2, $CHCl_3$) for (*R*)-**3j**.

synthesis can be considered to be more economical and environmentally friendly.[6] We have explored the use of microwaves in the pyrrole formation reaction. We tried different reaction conditions to carry out this reaction under microwave irradiation and found when the irradiation of chloroenone with amine compounds was carried out on the surface of silica gel without solvent the pyrroles were quickly furnished in good yield (Scheme 1). In a typical procedure, a mixture of chloroenone, amine compound and triethylamine adsorbed on the surface of silica gel was irradiated in a microwave oven for a certain period of time as required to complete the reaction. Elution of the reaction mixture with ether followed by the evaporation of solvent furnished the crude product which was purified by column chromatography. Conventional heating in dry media in place of microwave leads to a messy product with the formation of tarry material.

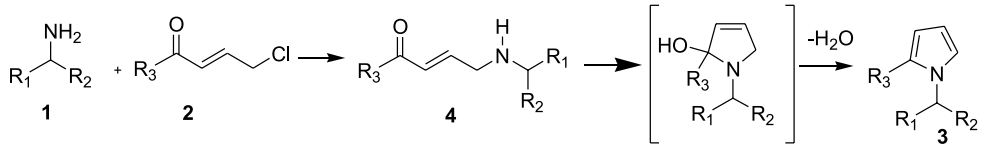


Scheme 1.

A wide range of chiral amine compounds were coupled with various chloroenones by this procedure through a single step operation to produce the corresponding alkyl substituted pyrroles as summarized in Table 1.

The reaction of alanine methyl ester (**1a**) with 5-chloro-3-pentene-2-one (**2a**) gave the 2-methylpyrrole derivative of alanine methyl ester (**3a**) in 79–80% yield. Under similar conditions 2-aminopropan-1-ol (**1d**) with **2a** gave the pyrrole derivative **3j** in 88–95% yield. The compound (*S*)-**3j** was also synthesized from the LAH reduction of (*S*)-**3a** in 81% yield. The pyrrole derivative **3j**, synthesized from different ways showed the same optical rotation value. This result showed that the formation of pyrrole derivative from alanine ester works without racemization.

The pyrrole derivative of amino acid esters and amino alcohols showed excellent separation properties by chiral HPLC column.[7] Control of the optical purity of the products by comparing racemic mixtures using chiral HPLC column



Scheme 2.

gave the same result as the formation of a pyrrole ring from amino acids esters in which no racemization occurs.

In general, the microwave assisted reactions are very fast and clean. The yields are reasonably good for a two-component coupling reaction. None of these operations involves any strong acid, base or solvent.

The suggested mechanism for the formation of pyrroles **3** is outlined in Scheme 2. It seems reasonable to suggest that the amine reacts initially with the allylic chloride to form **4** and the cyclisation onto the ketone occurs as the ring closing step, followed by elimination of water to give the product **3**.

3. Conclusion

In conclusion, the present microwave-assisted one-pot procedure provides an efficient methodology for the synthesis of alkyl-substituted pyrroles on the surface of silica gel from easily available starting materials by a condensation reaction. The notable advantages of this procedure are: (a) reasonably good yields; (b) fast reaction; (*c*) mild reaction conditions; (d) no racemization; (e) general applicability and (f) above all, green synthesis avoiding toxic reagents and solvents. Thus, it provides a better and more practical alternative to the existing methodologies.

4. Experimental

All reagents were of commercial quality and reagent quality solvents were used without further purification. IR spectra were determined on a Perkin Elmer 1600 spectrometer. NMR spectra were recorded on a Bruker DPX 400. Chemical shifts δ are reported in ppm relative to $CHCl_3$ (^{1}H: $\delta=7.27$), $CDCl_3$ (^{13}C: $\delta=77.0$) and CCl_4 (^{13}C: $\delta=96.4$) as internal standards. Column chromatography was conducted on silica gel 60 (40–63 μm). TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Merck), and the spots were visualized with UV light ($\lambda=254$ nm). Enantiomeric excesses were determined by HPLC analysis using a Thermo Finnigan Surveyor equipped with an appropriate chiral phase column. MS: Thermo Quest Finnigan multi Mass (EI, 70 eV). Optical rotations were measured with Krüss P3002RS automatic polarimeter. The reactions are carried out in Milestone-Start microwave instrument. Haloenones **2a–d** are synthesized according to the literature.[8]

4.1. Representative example

4.1.1. (*S*)-Methyl 2-(2-methyl-1*H*-pyrrol-1-yl)propanoate (*S*)-3a.[5b,c] A mixture of amine (103 mg, 1.0 mmol), chloroenone (153 mg, 1.3 mmol) and triethylamine (1.0 mmol) were uniformly adsorbed on the surface of silica gel (5 g) in a pyrex round bottomed flask at rt. The flask was then placed on a bed of silica gel in a porcelain basin and irradiated by a microwave oven at 500 W for 5 min (TLC). The reaction mass was eluted with ether and the ether extract was evaporated to leave the crude product which was purified by column chromatography over silica gel (EtOAc/hexane 1:2, 1:6 or 1:10) to afford the pure product as a viscous oil (133 mg, 79%). $[\alpha]_D^{20}=-49.4$ (*c* 2, CH_3OH), [lit.[5b] $[\alpha]_D^{20}=-48.1$(*c* 2, CH_3OH)]; IR(neat): ν 2897, 1778, 1463 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (d, $J=7.2$ Hz, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 4.80 (q, $J=7.0$, 1H, CH), 5.95 (m, 1H, =CH), 6.10 (m, 1H, =CH), 6.75 (m, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$):δ 12.4, 18.5, 53.1, 54.2, 108.2, 108.5, 118.0, 129.7, 173.3. The spectroscopic data are in accordance with the literature.[5b]

4.1.2. (*S*)-Methyl 2-(2-ethyl-1*H*-pyrrol-1-yl)propanoate (*S*)-3b. Light yellow oil (123 mg, 68%). $[\alpha]_D^{20}=-30.7$ (*c* 0.3, $CHCl_3$); IR ($CHCl_3$): ν 2954, 1742, 1434, 1203 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, $J=7.5$ Hz, 3H, CH_3), 1.60 (d, $J=7.2$ Hz, 3H, CH_3), 2.45 (q, $J=7.5$ Hz, 2H, CH_2), 3.62 (s, 3H, CH_3), 4.67 (q, $J=7.2$ Hz, 1H, CH), 5.78 (br s, 1H, =CH), 5.99 (t, $J=3.2$ Hz, 1H, =CH), 6.58 (br s, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.0, 18.3, 19.4, 52.3, 53.1, 105.3, 107.9, 117.1, 134.5, 171.6; MS (*m*/*z*) (rel abund): 181 [M^+] (13), 165 (32), 122 (80), 106 (65), 94 (100), 80 (51). Anal. Calcd for $C_{10}H_{15}NO_2$ (181.11): C, 66.27; H, 8.34; N, 7.73. Found: C, 66.15; H, 8.29; N, 7.85.

4.1.3. (*S*)-Ethyl 2-(2-ethyl-1*H*-pyrrol-1-yl)-4-(methylthio)butanoate (*S*)-3c. Yellow oil (209 mg, 82%). $[\alpha]_D^{20}=-46.0$ (*c* 0.4, $CHCl_3$); IR ($CHCl_3$): ν 2966, 1736, 1428, 1215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (m, 6H, CH_3), 1.99 (s, 3H, CH_3), 2.28 (m, 4H, CH_2), 2.51 (q, $J=7.5$ Hz, 2H, CH_2), 4.09 (m, 2H, CH_2), 4.78 (m, 1H, CH), 5.76 (br s, 1H, =CH), 6.00 (t, $J=3.2$ Hz, 1H, =CH), 6.56 (br s, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 14.1, 15.3, 19.5, 30.2, 31.6, 55.9, 61.3, 105.1, 108.3, 117.2, 135.2, 170.4; MS (*m*/*z*) (rel abund): 255 [M^+] (15), 180 (95), 152 (70), 134 (58), 108 (100), 93 (50). Anal. Calcd for $C_{13}H_{21}NO_2S$ (255.13): C, 61.14; H, 8.29; N, 5.48; S, 12.56. Found: C, 61.31; H, 8.22; N, 5.56; S, 12.43.

4.1.4. (*S*)-Ethyl 2-(2-methyl-1*H*-pyrrol-1-yl)-4-(methylthio)butanoate (*S*)-3d. Yellow oil (169 mg, 70%). $[\alpha]_D^{20}=-39.5$ (*c* 0.8, $CHCl_3$); IR ($CHCl_3$): ν 2978, 2910, 1738, 1420, 1295 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, $J=7.2$ Hz, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.31 (m, 4H, CH_2), 4.11 (m, 2H, CH_2), 4.78 (m, 1H, CH), 5.74 (br s, 1H, =CH), 5.96 (m, 1H, =CH), 6.54 (m, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2, 14.2, 15.3, 30.1, 31.2, 56.1, 61.4, 107.1, 108.3, 117.2, 128.9,

170.4; MS (*m*/*z*) (rel abund): 241 [M^+] (13), 196 (5), 166 (84), 137 (57), 120 (91), 94 (100), 80 (40). Anal. Calcd for $C_{12}H_{19}NO_2S$ (241.11): C, 59.72; H, 7.93; N, 5.80; S, 13.29. Found: C, 59.64; H, 8.06; N, 5.71; S, 13.16.

4.1.5. (*S*)-Ethyl 2-(2-cyclohexyl-1*H*-pyrrol-1-yl)-4-(methylthio)butanoate (*S*)-3e. Dark yellow oil (229 mg, 74%). $[\alpha]_D^{20} = -34.8$ (*c* 0.6, $CHCl_3$); IR ($CHCl_3$): ν 2927, 1735, 1444, 1211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (t, $J=7.5$ Hz, 3H, CH_3), 1.30 (m, 4H, CH_2), 1.75 (m, 6H, CH_2), 1.99 (s, 3H, CH_3), 2.17 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 2.45 (m, 1H, CH), 4.10 (m, 2H, CH_2), 4.81 (m, 1H, CH), 5.75 (m, 1H, =CH), 5.99 (m, 1H, =CH), 6.51 (m, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 15.3, 26.2, 26.7, 26.8, 30.3, 31.9, 33.8, 34.3, 35.4, 55.8, 61.3, 103.8, 108.4, 116.8, 139.5, 170.5; MS (*m*/*z*) (rel abund): 309 [M^+] (8), 292 (13), 260 (14), 234 (67), 205 (21), 191 (34), 179 (80), 166 (82), 152 (59), 147 (34), 118 (55), 106 (100), 81 (27). Anal. Calcd for $C_{17}H_{27}NO_2S$ (309.18): C, 65.98; H, 8.79; N, 4.53; S, 10.36. Found: C, 66.12; H, 8.67; N, 4.45; S, 10.44.

4.1.6. (*S*)-Ethyl 2-(2-ethyl-1*H*-pyrrol-1-yl)-3-hydroxypropanoate (*S*)-3g. Light yellow oil (162 mg, 77%). $[\alpha]_D^{20} = -27.1$ (*c* 0.6, $CHCl_3$); IR ($CHCl_3$): ν 3451, 2973, 2927, 1735, 1479, 1287 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (m, 6H, CH_3), 2.48 (q, $J=7.5$ Hz, 2H, CH_2), 2.53 (br s, 1H, OH), 3.80 (m, 1H, CH_A), 3.98 (m, 1H, CH_B), 4.10 (m, 2H, CH_2), 4.63 (t, $J=6.7$ Hz, 1H, CH), 5.78 (m, 1H, =CH), 5.98 (t, $J=3.2$ Hz, 1H, =CH), 6.56 (m, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.1, 14.1, 19.4, 59.3, 61.6, 63.0, 105.3, 108.3, 117.7, 135.3, 169.5; MS (*m*/*z*) (rel abund): 211 [M^+] (15), 195 (38), 137 (38), 106 (55), 94 (100), 80 (82). Anal. Calcd for $C_{11}H_{17}NO_3$ (211.12): C, 62.54; H, 8.11; N, 6.63. Found: C, 62.49; H, 8.24; N, 6.54.

4.1.7. (*R*)-2-Ethyl-1-(1-phenylethyl)-1*H*-pyrrole (*R*)-3o. Light yellow oil (167 mg, 84%). $[\alpha]_D^{20} = -20.7$ (*c* 0.4, $CHCl_3$); IR ($CHCl_3$): ν 3055, 2985, 2927, 1450, 1211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, $J=7.5$ Hz, 3H, CH_3), 1.70 (d, $J=7.1$ Hz, 3H, CH_3), 2.23 (m, 1H, CH_A), 2.40 (m, 1H, CH_B), 5.17 (q, $J=7.1$ Hz, 1H, CH), 5.82 (br s, 1H, =CH), 6.02 (t, $J=3.2$ Hz, 1H, =CH), 6.66 (m, 1H, =CH), 7.00 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.0, 19.6, 22.7, 54.5, 105.3, 107.1, 116.9, 125.3, 125.6, 127.1, 128.6, 135.0, 144.1; MS (*m*/*z*) (rel abund): 199 [M^+] (15), 105 (100), 95 (67), 80 (93). Anal. Calcd for $C_{14}H_{17}N$ (199.14): C, 84.37; H, 8.60; N, 7.03. Found: C, 84.23; H, 8.56; N, 7.15.

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References and notes

1. Ragno, R.; Marshall, G. R.; Di Santo, R.; Costi, R.; Massa, S.; Rompei, R.; Artico, M. *Bioorg. Med. Chem.* **2000**, *8*, 1423. (b) Franc, C.; Denone, F.; Cuisinier, C.; Ghosez, L. *Tetrahedron Lett.* **1999**, *40*, 4555. (c) Liu, J.; Yang, Q.; Mak, T. C.; Wong, H. N. C. *J. Org. Chem.* **2000**, *65*, 3587. (d) Caldarelli, M.; Habermann, J.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1999**, 107. (e) Haubmann, C.; Hubner, H.; Gmeiner, P. *Bioorg. Med. Chem. Lett.* **1999**, *21*, 3143. (f) Khanna, I. K.; Weier, R. M.; Yu, Y.; Collins, P. W.; Miyashiro, J. M.; Koboldt, C. M.; Veenhuizen, A. W.; Currie, J. L.; Seibert, K.; Isakson, P. C. *J. Med. Chem.* **1997**, *11*, 1619. (g) Dieter, R. K.; Yu, H. *Org. Lett.* **2000**, *2*, 2283.
2. Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1999**, *20*, 2849.
3. (a) Jefford, C. W.; Tang, Q.; Zaslona, A. *J. Am. Chem. Soc.* **1991**, *113*, 3513. (b) Wasserman, H. H.; Vu, C. B.; Cook, J. D. *Tetrahedron* **1992**, *48*, 2101. (c) Rassu, G.; Carta, P.; Pinna, L.; Battistini, L.; Zanardi, F.; Acquotti, D.; Casiraghi, G. *Eur. J. Org. Chem.* **1999**, 1395. (d) Nemr, A. E. *Tetrahedron* **2000**, *56*, 8579. (e) Jefford, C. W. *Curr. Org. Chem.* **2000**, *4*, 205.
4. (a) Jefford, C. W.; Naide, F.; Sienkiewicz, de V.K. *Tetrahedron: Asymmetry* **1996**, *7*, 1069. (b) Grigg, R.; Yoganathan, G. *Tetrahedron: Asymmetry* **1996**, *7*, 273. (c) Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocyclic Chemistry*, *Vol. 4*; Pergamon: Oxford, 1994. (d) Baltazzi, B.; Kirmen, L. I. *Chem. Rev.* **1963**, *63*, 511. (e) Earle, M. J.; Heaney, H. *Synlett* **1992**, 745.
5. (a) Demir, A. S.; Akhmedov, I. M.; Sesenoglu, O. *Tetrahedron* **2002**, *58*, 9793. (b) Demir, A. S.; Akhmedov, I. M.; Sesenoglu, O.; Alpturk, O.; Apaydin, S.; Gercek, Z.; Ibrahimzade, N. *J. Chem. Soc. Perkin Trans. 1* **2001**, 1162. (c) Demir, A. S.; Akhmedov, I. M.; Tanyeli, C.; Gercek, Z.; Gadzhili, R. A. *Tetrahedron: Asymmetry* **1997**, *8*, 753. (d) Aydogan, F.; Demir, A. S. *Tetrahedron: Asymmetry* **2004**, *15*, 259. (e) Demir, A. S.; Aydogan, F.; Akhmedov, I. M. *Tetrahedron: Asymmetry* **2002**, *13*, 601.
6. (a) Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J.-L.; Petit, A. *Tetrahedron* **1999**, *55*, 10851. (b) Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199 and references therein. (c) Alexandre, F.-R.; Berecibar, A.; Wrigglesworth, R.; Besson, T. *Tetrahedron Lett.* **2003**, *44*, 4455. (d) Jiao, G.-S.; Castro, J. C.; Thorensen, L. H.; Burgess, K. *Org. Lett.* **2003**, *5*, 3675. (e) Paul, S.; Gupta, M.; Gupta, R.; Loupy, A. *Synthesis* **2002**, 75. (f) De La Hoz, A.; Diaz-Ortiz, A.; Langa, F. In *Microwaves in Organic Synthesis*; Loupy, A., Ed.; Wiley-VCH: Germany, 2003. (g) Cheng, Q.; Zhang, W.; Tagami, Y.; Oritani, T. *J. Chem. Soc. Perkin Trans. 1* **2001**, 452. (h) Rao, H. S. P.; Jothilingam, S. *Tetrahedron Lett.* **2001**, *42*, 6595.
7. Optical purity is determined by chiral HPLC analysis (Chiral pack AD column, UV detection at 220 nm, 90/10 *i*-hexane/isopropanol, flow rate 0.75 ml/min).
8. Barbry, D.; Faven, C.; Ajana, A. *Synth. Commun.* **1993**, *23*(19), 2647. (b) Ibragimov, I. I.; Mamedov, E. I.; Ismailov, A. T.; Aliev, A. G.; Mekhtieva, Sh. Z.; Dzhafarov, V. G.; Belyaeva, V. I. *Zhurnal Organicheskoi Khimii* **1990**, *26*(8), 1648. (c) Ibragimov, E. I.; Ismailov, A. T.; Mekhtieva, Sh. Z.; Mamedov, N. N.; Belyaeva, V. I. *Zhurnal Organicheskoi Khimii* **1990**, *26*(11), 2294.