

Highly Regioselective *N*-Alkylation of Benzotriazole under Solvent-Free Conditions

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An efficient, simple and solvent-free method for highly regioselective *N*-alkylation of benzotriazole in the presence of SiO₂, K₂CO₃ and tetrabutylammonium bromide (TBAB) under thermal and microwave conditions has been described. In this method, 1-alkyl benzotriazoles were obtained regioselectively in moderate to high yields and short reaction times.

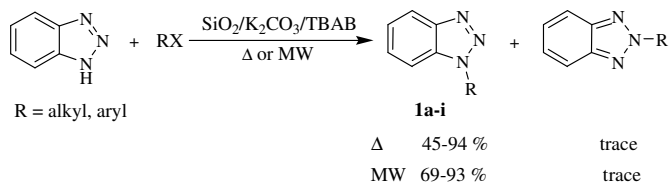
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INTRODUCTION

Solvent-free organic reactions have been applied as an useful protocol in organic synthesis [1]. Solid-state technique under thermal or microwave conditions often leads to shorter reaction times, increased yields, easier workup, matches with green chemistry protocols, and may enhance the regio- and stereoselectivity of reactions [1].

1-Alkyl benzotriazoles are very important compounds as they have various biological activities [2]. This class of compounds has been used as herbicides [2a,b], insecticides [2a,b], acaricides [2a,b], and receptors [2c] and moreover, they have been used in many organic transformations [3]. Different bases and reagents are used for *N*-alkylation of benzotriazole, such as sodium ethoxide [4a], potassium *t*-butoxide [4b], potassium hydroxide [4c], KF/Al₂O₃ [4d,e], excess amounts of benzotriazole as a base [4f], NCS/PPh₃ [4g], Pd(PPh₃)₄ [4h], Pd/Cu(II)/base [4i,j], Cu(OAc)₂/NaH [4k] and sodium

hydroxide (in ionic liquid) [4l]. Most of these methods are associated with several drawbacks. The major drawback in *N*-alkylation of benzotriazole is low regioselectivity [4a-e,4i-1,5]. Other disadvantages like lack of simplicity [4i,j] and long reaction time [4f,g,k] are still observed. However, the 1-alkyl derivatives of benzotriazole have more significance rather than its *N*²-analogs from different aspects [2,3]. To the best of our knowledge, a few endeavors have been achieved for highly regioselective preparation of *N*¹-isomers. Considering these aspects and also in extension of our previous studies on solvent-free organic reactions [6], herein, we report an efficient, clean and solvent-free method for highly



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regioselective *N*-alkylation of benzotriazole under thermal and microwave irradiation conditions in the presence of SiO₂, K₂CO₃ and tetrabutylammonium bromide (Scheme 1).

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were obtained from Merck or Fluka chemical companies. The known compounds were identified by the comparison of their melting points and ¹H NMR with the authentic samples. The progress of the reactions was followed by TLC using silica-gel SILG/UV 254 plates. Silica gel 60, 0.063-0.200 mm (70-230 mesh ASTM) was used for column chromatography and support. The ¹H NMR and ¹³C NMR were run on a Bruker Avanced DPX-250 FT-NMR spectrometer. Mass spectra were recorded on a Shimadzu GC MS-QP 1000 EX apparatus. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes and are uncorrected. A MB 245 domestic microwave oven from Butan Industrial Co. (Tehran, Iran) was used.

General Procedure for Highly Regioselective *N*-Alkylation of Benzotriazole under Thermal and Microwave Conditions

To a well ground mixture of benzotriazole (1.19 g, 10 mmol), SiO₂ (3.50 g), K₂CO₃ (1.38 g, 10 mmol) and TBAB (3.22 g, 10 mmol) in a test tube was added the alkylating agent (18 and 14 mmol in thermal and microwave conditions, respectively) and mixed carefully with a small rod. It should be noted that, in the case of solid alkylating agents (Table 3, entry 10 and Table 4, entry 1), they were thoroughly mixed with other reactants in a mortar to give a homogeneous mixture. Then, the test tube was immersed in an oil bath for the appropriate reaction time and temperature, or exposed to microwave irradiation for the appropriate time and the power. Then, the reaction mixture was cooled to room temperature and chloroform (250 ml) was added. The resulting precipitate was filtered and the filtrate was washed with water (2 × 200 ml) and dried over anhydrous MgSO₄. The solvent was evaporated and the crude product was purified by column chromatography on silica gel with EtOAc/*n*-hexane (1/5 to 1/2).

Ethyl 2-(1*H*-1,2,3-benzotriazol-1-yl)acetate (1a). Column

chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave colorless crystals; m.p.: 75-77 °C (Lit. [4f] 74-78 °C).

1-Benzyl-1*H*-1,2,3-benzotriazole (1b). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave colorless crystals; m.p.: 113-114 °C (Lit. [4a] 114-116 °C).

1-(2-Methylbenzyl)-1*H*-1,2,3-benzotriazole (1c). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave colorless crystals; m.p.: 82-83 °C (Lit. [4a] 84-85 °C).

1-Methyl-1*H*-1,2,3-benzotriazole (1d). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/4) gave colorless crystals; m.p.: 62-63 °C (Lit. [4g] 64-65 °C).

1-Hexyl-1*H*-1,2,3-benzotriazole (1e). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave pale yellow oil (Lit. [4g] oil).

1-Allyl-1*H*-1,2,3-benzotriazole (1f). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave pale yellow oil (Lit. [4g] oil).

1-(2-Propynyl)-1*H*-1,2,3-benzotriazole (1g). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/5) gave colorless crystals; m.p.: 57-58 °C (Lit. [4g] 57 °C).

1-(2,4-Dinitrophenyl)-1*H*-1,2,3-benzotriazole (1h). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/3) gave yellow crystals; m.p.: 180-182 °C (Lit. [4f] 182-184 °C).

1-(2-Pyridyl)-1*H*-1,2,3-benzotriazole (1i). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/4) gave pale yellow crystals; m.p.: 109-111 °C (Lit. [4f] 108-111 °C).

1-(2-{2-[2-(1*H*-1,2,3-Benzotriazol-1-yl)ethoxy]ethoxy}ethyl)-1*H*-1,2,3-benzotriazole (2a). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/2) gave colorless crystals; m.p.: 97-98 °C; ¹H NMR (250 MHz, DMSO-*d*₆): δ 3.34 (s, 4H), 3.76 (t, *J* = 4.8 Hz, 4H), 4.74 (t, *J* = 4.8 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 47.7, 67.3, 71.1, 109.5, 117.6, 120.2, 128.2, 133.3, 145.1; MS (*m/z*): 352 (*M*⁺).

1-(2-{2-[2-(2*H*-1,2,3-Benzotriazol-2-yl)ethoxy]ethoxy}ethyl)-1*H*-1,2,3-benzotriazole (3a). Column chromatography

on silica gel eluted with EtOAc/*n*-hexane (1/2) gave pale yellow oil; ¹H NMR (250 MHz, DMSO-*d*₆): δ 3.20 (s, 4H), 3.61 (t, *J* = 4.8 Hz, 2H), 3.75 (t, *J* = 4.8 Hz, 2H), 4.55-4.64 (complex, 4H), 7.12-7.28 (complex, 4H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 47.7, 55.9, 68.4, 68.9, 69.5, 110.8, 117.7, 119.3, 123.6, 126.1, 126.8, 133.3, 143.7, 145.2; MS (*m/z*): 352 (M⁺).

1-[2-(2-{2-[2-(1*H*-1,2,3-Benzotriazol-1-yl)ethoxy]ethoxy}ethyl)-1*H*-1,2,3-benzotriazole (2b). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/2) gave pale yellow oil; ¹H NMR (250 MHz, DMSO-*d*₆): δ 2.99 (t, *J* = 4.4 Hz, 4H), 3.11 (t, *J* = 4.4 Hz, 4H), 3.65 (t, *J* = 4.5 Hz, 4H), 4.63 (t, *J* = 4.5 Hz, 4H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 47.8, 68.5, 69.6, 110.9, 118.8, 123.1, 126.8, 133.3, 145.2; MS (*m/z*): 396 (M⁺).

1-[2-(2-{2-[2-(2*H*-1,2,3-Benzotriazol-2-yl)ethoxy]ethoxy}ethyl)-1*H*-1,2,3-benzotriazole (3b). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/2) gave pale yellow oil; ¹H NMR (250 MHz, DMSO-*d*₆): δ 2.91 (t, *J* = 4.5 Hz, 4H), 3.07 (t, *J* = 4.5 Hz, 4H), 3.57 (t, *J* = 4.8 Hz, 2H), 3.66 (t, *J* = 4.8 Hz, 2H), 4.48 (t, *J* = 4.8 Hz, 2H), 4.55 (t, *J* = 4.8 Hz, 2H), 7.10-7.21 (complex, 4H), 7.50 (d, *J* = 8.1 Hz, 1H); 7.73 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (62.5 MHz, DMSO-*d*₆): δ 48.0, 68.9, 69.4, 70.0, 70.4, 110.1, 117.5, 118.7, 124.3, 125.4, 127.1, 133.3, 143.4, 145.0; MS (*m/z*): 396 (M⁺).

1-[14-(1*H*-1,2,3-Benzotriazol-1-yl)-3,6,9,12-tetraoxatetradecyl]-1*H*-1,2,3-benzotriazole (2c). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/2.5) gave pale yellow oil; ¹H NMR (250 MHz, CDCl₃): δ 2.91-3.06 (complex, 12H), 3.66 (t, *J* = 4.7 Hz, 4H), 4.59 (t, *J* = 4.7 Hz, 4H), 7.18-7.29 (complex, 4H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (62.5 MHz, CDCl₃): δ 47.4, 66.9, 70.1, 70.8, 71.0, 110.6, 118.2, 120.5, 127.8, 133.4, 144.9; MS (*m/z*): 440 (M⁺).

2-[14-(2*H*-1,2,3-Benzotriazol-2-yl)-3,6,9,12-tetraoxatetradecyl]-1*H*-1,2,3-benzotriazole (3c). Column chromatography on silica gel eluted with EtOAc/*n*-hexane (1/2.5) gave pale yellow oil; ¹H NMR (250 MHz, CDCl₃): δ 2.89-3.03 (complex, 12H), 3.49 (t, *J* = 4.7 Hz, 2H), 3.60 (t, *J* =

4.7 Hz, 2H), 4.42 (t, *J* = 4.7 Hz, 2H), 4.49 (t, *J* = 4.7 Hz, 2H), 7.11-7.23 (complex, 4H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (62.5 MHz, CDCl₃): δ 47.5, 54.5, 67.9, 68.5, 68.9, 69.1, 69.3, 109.8, 117.1, 118.9, 124.1, 125.8, 126.5, 133.3, 143.2, 145.4; MS (*m/z*): 440 (M⁺).

RESULTS AND DISCUSSION

To optimize the reaction conditions, we have studied the synthesis of compound **1a** as a model reaction under thermal and microwave conditions as follows (Scheme 1). A well ground mixture of benzotriazole, ethyl bromoacetate, K₂CO₃ and TBAB was heated in an oil bath (120 °C) for 40 min. Here, a moderate yield and selectivity were obtained even by increasing the reaction time and temperature. Similar results were obtained under microwave irradiation (200 W). In this case, the yield and selectivity were remarkably improved when silica gel was added to the reaction media (Table 1). Other supports were also examined in the reaction, among which silica gel showed the best results (Table 1). The optimum amount of silica gel for *N*-alkylation of 10 mmol of benzotriazole in thermal and microwave conditions was found to be 3.5 g.

To select the suitable base for the reaction, the effect of various inorganic and organic bases in the presence of SiO₂ and TBAB was examined (Table 2). Higher yields and selectivities as well as shorter reaction times were obtained under thermal and microwave conditions when K₂CO₃ was elaborated.

In another study, the role of TBAB was evaluated in both reaction conditions. The absence of TBAB in the reaction media resulted in low reaction yields, even at prolong reaction time and higher reaction temperature or the microwave power. The use of catalytic amount of TBAB caused negligible improvement in the efficiency of the reaction. The optimal amount of TBAB was found to be 1 equivalent of TBAB was used under both conditions.

To realize the capability of the present method in comparison to reported methods for *N*-alkylation of benzotriazole, we have examined the synthesis of compounds **1a-1i** with the reported methods. The results are summarized in Table 3, which indicate that the present method is more

Table 1. The Effect of Supports on *N*-Alkylation of Benzotriazole with Ethyl Bromoacetate under Thermal (Δ , 120 °C) and Microwave (MW, 200 W) Conditions

Entry	Support	Time (min)		Yield (%) ^a	
		Δ	MW	Δ	MW
1 ^b	-	40	5	56	53
2 ^c	Silica gel	15	1	90	82
3	Neutral alumina	30	3	76	74
4	Basic alumina	30	3	75	74
5	Clay	40	4	70	68
6	Molecular sieve	40	4	66	63

^aIsolated yield of *N*¹-isomer. ^bWithout support. ^cIn this case, the yield of *N*²-isomer under both conditions was trace.

Table 2. The Effect of Different Bases on Reaction of Benzotriazole with Ethyl Bromoacetate under Thermal (Δ , 120 °C) and Microwave (MW, 200 W) Conditions

Entry	Base	Time (min)		Yield (%) ^a	
		Δ	MW	Δ	MW
1 ^b	-	60	6	27	30
2 ^c	K ₂ CO ₃	15	1	90	82
3	Cs ₂ CO ₃	15	1	73	66
4	NaOH	20	1	38	36
5	<i>t</i> -BuOK	20	1	45	41
6	CaO	60	7	16	18
7	DABCO	60	4	25	23
8	DMAP	60	4	22	22

^aIsolated yield of *N*¹-isomer. ^bWithout base. ^cIn this case, the yield of *N*²-isomer under both conditions was trace.

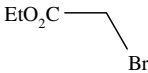
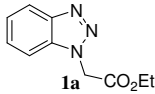
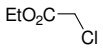
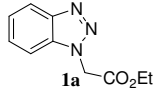
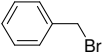
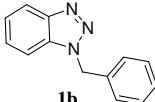
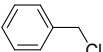
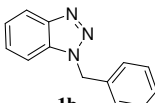
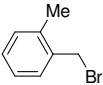
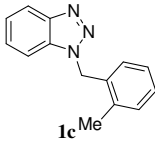
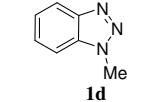

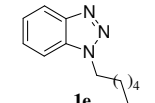

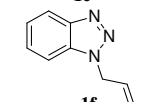

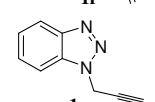
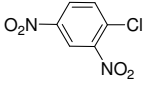
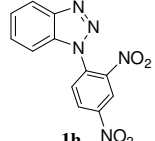

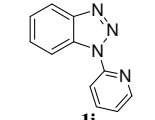
Table 3. The Comparative Synthesis of Compounds **1a-1i** Using the Reported Methods *vs.* the Present Method

Entry	Product	Reported method		Present method	
		Time (h)	Yield (%)	Time (min)	Yield ^a (%)
1	1a	0.74	73 [4f]	15	90
2	1b	61	81 [4f]	20	89
3	1c	3	85 [4a]	20	90
4	1d	24	60 [4g]	1	74
5	1e	24	60 [4g]	3	84
6	1f	24	75 [4g]	1	87
7	1g	24	80 [4g]	2	85
8	1h	108	96 [4f]	25	94
9	1i	18	99 [4f]	6	89

^aIsolated yield.

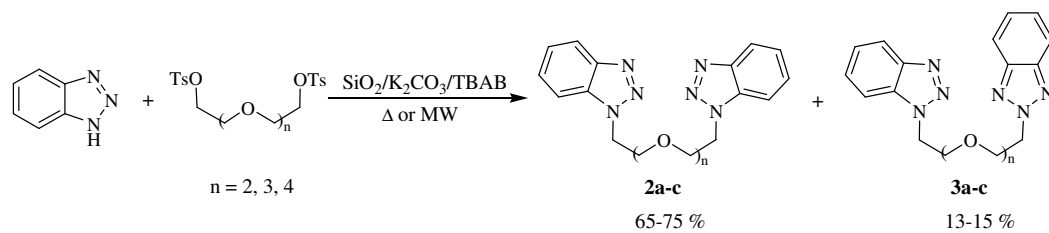
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Table 4. *N*-Alkylation of Benzotriazole (BtH) in the Presence SiO₂, K₂CO₃ and TBAB under Solvent-Free Thermal (Δ) and Microwave (MW) Conditions

Entry	RX	Product ^a	Time (min)		T (°C) ^b	MW power (W)	Yield (%) ^c	
			Δ	MW			Δ	MW
1		 1a	15	1	120	200	90	82
2		 1a	15	1	120	200	68	75
3		 1b	20	2	140	200	89	73
4		 1b	25	2	90	200	53	69
5		 1c	20	2	140	200	90	75
6	Me ₂ SO ₄	 1d	15	1	70	100	55	74
7		 1e	40	3	150	300	47	84
8 ^d		 1f	25	1	65	200	56	87
9 ^d		 1g	30	2	50	200	45	85
10		 1h	25	5	150	200	94	93
11		 1i	30	6	150	300	N.R. ^e	89

^aIn all cases, the yield of *N*²-isomer was negligible (*N*¹/*N*² > 22/1). ^bReaction temperature in thermal method.

^cIsolated yield of *N*¹-isomer. ^dIn this reaction, RX/BtH (mol/mol) = 3/1. ^eNo reaction.

Table 5. The Reaction of Benzotriazole (BtH) with Ditosylates in the Presence of SiO₂, K₂CO₃ and TBAB under Solvent-Free Thermal (150 °C) and Microwave (300 W) Conditions

Entry	RX ^a	Product	Time (min)		Yield (%) ^b	
			Δ	MW	Δ	MW
1					71	75
			60	4	14	15
2					69	72
			70	5	15	15
3					65	68
			70	5	13	14

^aROTs/BtH (mol/mol) = 1/3. ^bIsolated yield.

efficient.

To investigate the versatility as well as selectivity of the method, the reactions were examined with various structurally diverse alkyl and aryl halides under thermal and microwave conditions (Tables 4 and 5). As it is shown in Tables 4 and 5, the reactions proceeded with high regioselectivity under both conditions, and the desired 1-alkyl benzotriazoles were obtained in moderate to high yields. The N^1/N^2 (mol/mol) ratios for aliphatic alkylating agents were found to be in the range 22/1 to 29/1.

As Tables 4 and 5 show, for *N*-alkylation of benzotriazole with benzyl bromides, ethyl bromoacetate and 1-chloro-2,4-dinitrobenzene, the thermal method was more efficient. However, in *N*-alkylation with ethyl chloroacetate, dimethyl sulfate, *n*-hexyl iodide, allyl bromide, propargyl chloride, 2-chloropyridine and ditosylates the microwave method was found to be more suitable. In addition, the regioselectivity of the reaction under microwave conditions was higher in comparison with that of the thermal protocol.

As expected, alkyl bromides were reacted with benzotriazole in higher yields than alkyl chlorides under both reaction conditions (Table 4, entries 1-4). This can be rationalized to higher reactivity of alkyl bromides rather than alkyl chlorides as well as higher boiling points of the bromo derivatives relative to chloro compounds which cause less evaporation during the temperature enhancement. The lower yields obtained for 1-allyl and 1-propargyl benzotriazole in thermal method (56% and 45 %, respectively) in comparison with microwave method (87% and 85%, respectively) can be related to the low boiling points of allyl bromide (b.p.: 70 °C) and propargyl chloride (b.p.: 57 °C). *N*-Substitution of benzotriazole with aryl halides afforded only N^1 -isomers (Table 4, entries 10-11). *N*-Alkylation of benzotriazole with ditosylates proceeded smoothly to produce two alkylated isomers in high total yields (Table 5). Furthermore, when polyethylene glycol ditosylates were used instead of alkyl halides in the reaction, the selectivity was slightly decreased.

CONCLUSIONS

In conclusion, the presented procedures provide a clean, simple and efficient solvent-free methodology for easy and selective preparation of various 1-alkyl benzotriazoles with

moderate to good yields using cheap and safe reagents under thermal and microwave conditions.

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REFERENCES

- [1] a) K. Tanaka, Solvent-free Organic Synthesis, Wiley-VCH, Weinheim, 2004; b) A. Loupy, Microwave in Organic Synthesis, Wiley-VCH, Weinheim, 2004.
- [2] a) R.E. Deal, R.V. Kendall, Jpn. Kokai. (1978) 78121762, Chem. Abstr. 90 (1979) 98559; b) American Cyanamid Co. Belg. Patent (1977) 853179, Chem. Abstr. 88 (1978) 190843; c) J.L. Mokrosz, M.H. Paluchowska, E. Chojnacka-Wojcik, M. Filip, S. Charakchieva-Minol, A. Deren-Wesolek, M.J. Mokrosz, J. Med. Chem. 37 (1994) 2754; d) A.R. Katritzky, A.F. Pozharskii, Handbook of Heterocyclic Chemistry, 2th ed., Pergamon, New York, 2000; e) T. Eicher, S. Hauptmann, The Chemistry of Heterocycles, Structures, Reactions, Synthesis and Applications, Wiley-VCH, GmbH and Co KGaA, Weinheim, 2003.
- [3] a) A.R. Katritzky, B.V. Rogovoy, Chem.-Eur. J. 9 (2003) 4586; b) W. Peczynska-Czoch, F. Pognan, L. Kaczmarek, J. Boratynsky, J. Med. Chem. 37 (1994) 2503.
- [4] a) M.S. Gibson, J. Chem. Soc. (1956) 1076; b) J. Bergman, P. Sand, Tetrahedron Lett. 25 (1984) 1957; c) L.J. Mathias, D. Burkett, Tetrahedron Lett. 20 (1979) 4709; d) H. Zhang, T. Hu, Y. Zhang, Q. Chen, Xiamen Daxue Xuebao, Ziran Kexuebao 38 (1999) 418 (Ch); e) H. Zhang, Zhang, T. Hu, Q. Chen, Xiamen Daxue Xuebao, Ziran Kexuebao 38 (1999) 76 (Ch); f) A.R. Katritzky, J. Wu, Synthesis (1994) 597; g) A.R. Katritzky, D.C. Oniciu, I. Ghiriviga, Synth. Commun. 27 (1997) 1613; h) N. Arnau, Y. Arredona, M. Moreno-Mañas, R. Pleixats, M. Villarroja, J. Heterocyc. Chem.

- 32 (1995) 1325; i) I.P. Beletskaya, D.V. Davydov, M. Moreno-Mañas, *Tetrahedron Lett.* 39 (1998) 5621; j) I.P. Beletskaya, D.V. Davydov, M. Moreno-Mañas, *Tetrahedron Lett.* 39 (1998) 5617; k) P. López-Alvarado, C. Avendaño, J.C. Menéndez, *J. Org. Chem.* 60 (1995) 5678; l) Z.-G. Le, Z.-C. Chen, Y. Hu, Q.-G. Zheng, *J. Chem. Res.* (2004) 344.
- [5] a) N. L. Miller, E.C. Wagner, *J. Am. Chem. Soc.* 76 (1954) 1847; b) K. Sukata, *Bull. Chem. Soc. Jpn.* 56 (1983) 280; c) M. Märky, H. Schmid, H.-J. Hansen, *Helv. Chim. Acta* 62 (1979) 2129.
- [6] a) A. Khalafi-Nezhad, A. Parhami, M.N. Soltani Rad, A. Zare, *Tetrahedron Lett.* 46 (2005) 6879; b) A. Khalafi-Nezhad, A. Zare, M.N. Soltani Rad, B. Mokhtari, A. Parhami, *Synthesis* (2005) 419; c) A. Khalafi-Nezhad, B. Mokhtari, *Tetrahedron Lett.* 45 (2004) 6737; d) A. Khalafi-Nezhad, M.N. Soltani Rad, A. Khoshnood, *Synthesis* (2004) 583; e) A. Khalafi-Nezhad, M.N. Soltani Rad, G.H. Hakimelahi, *Helv. Chim. Acta* 86 (2003) 2396; f) A. Khalafi-Nezhad, B. Mokhtari, M.N. Soltani Rad, *Tetrahedron Lett.* 44 (2003) 7325; g) A. Khalafi-Nezhad, F. Alamdari, N. Zekri, *Tetrahedron* 56 (2000) 7503; h) A. Khalafi-Nezhad, A. Hashemi, *J. Chem. Res., Synop* (1999) 720.