Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

Silica-supported bismuth(III) chloride as a new recyclable heterogeneous catalyst for the Paal—Knorr pyrrole synthesis

Kioumars Aghapoor¹, Leila Ebadi-Nia¹, Farshid Mohsenzadeh¹, Mina Mohebi Morad¹, Yadollah Balavar¹, Hossein Reza Darabi^{*}

Nano & Organic Synthesis Lab., Chemistry & Chemical Engineering Research Center of Iran, Pajoohesh Blvd., km 17, Karaj Hwy, Tehran 14968-13151, Iran

ARTICLE INFO

Article history: Received 10 September 2011 Received in revised form 7 January 2012 Accepted 8 February 2012

Keywords: BiCl₃/SiO₂ Heterogeneous Lewis acid catalyst Paal–Knorr reaction Pyrrole

ABSTRACT

Silica-supported bismuth(III) chloride (BiCl₃/SiO₂) acts as a highly efficient heterogeneous Lewis acid catalyst for the Paal–Knorr pyrrole synthesis in hexane at room temperature. The catalyst exhibited remarkable reusable activity and higher catalytic performance than homogeneous BiCl₃. A plausible mechanism for the catalytic action of BiCl₃/SiO₂ has been introduced.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous supported catalysts have been gained much attention in recent years, as they possess a number of advantages [1,2]. Immobilization of catalysts on solid support provides an ideal method for combining the advantages of homogeneous catalysts (high activity and selectivity, etc.) with the engineering advantages of heterogeneous catalysts (available active site, easy catalyst separation, long catalytic life, thermal stability, low hygroscopic properties, easy handling and reusability of catalysts). Therefore, use of supported and recoverable catalysts in organic transformations has economical and environmental benefits [3–8].

Pyrroles are important heterocyclic compounds displaying remarkable pharmacological properties such as antibacterial, antiviral, anti-inflammatory, antitumoral, and antioxidant activities [9-11]. The pyrrole moiety is also present in many naturally occurring compounds such as heme, chlorophyll, and vitamin B₁₂ [12–17]. In view of their high significance, many methodologies have been developed for the construction of the pyrrole moiety regarded as skeleton. Among them, the Paal–Knorr synthesis

remains the most useful preparative method for generating pyrroles [18–28]. In this method, 1,4-dicarbonyl compounds are converted to pyrrole via acid-mediated dehydrative cyclization in the presence of a primary amine [29,30]. The main limitations to intensive use of this reaction are the strong reaction conditions required for cyclization (use of boiling acetic acid for extended times).

Recently, a range of catalysts and protocols have been developed for the preparation of these compounds, e.g. alumina [31], montmorillonite KSF [32,33], iodine [33], montmorillonite K-10 \pm microwave irradiation [34,35], Fe³⁺-montmorillonite [36], layered α -Zr(KPO₄)₂ [37], [bmim]I ionic liquid [38], Sc(OTf)₃ [39], microwave irradiation [40], ZrCl₄/ultrasonic irradiation [41], InCl₃ [42] and Ga(OTf)₃ [43].

The importance of bismuth as a homogeneous catalyst has already been cited in the literature for the Paal–Knorr synthesis [44,45]. The aim of the present work is the incorporation of bismuth into the framework of silica, combining the properties such as catalyst selectivity and activity with the ease of separation and catalyst reuse.

In the continuation of our studies on the design and application of solid acid catalysts in organic transformations [46,47], herein, we wish to introduce silica-supported bismuth(III) chloride (BiCl₃/ SiO₂) as a novel heterogeneous catalyst for the Paal–Knorr pyrrole cyclocondensation reaction (Scheme 1).



^{*} Corresponding author. Tel.: +98 21 44580720; fax: +98 21 44580762.

E-mail addresses: darabi@ccerci.ac.ir, r_darabi@yahoo.com (H.R. Darabi).

¹ Tel.: +98 21 44580720; fax: +98 21 44580762.

⁰⁰²²⁻³²⁸X/\$ – see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2012.02.008



Scheme 1. Condensation of hexane-2,5-dione with amines catalyzed by BiCl₃/SiO₂.

2. Experimental

2.1. Materials and methods

The N₂ adsorption/desorption analyses were performed on BELSORP-minill at 77 K. Silica gel was degassed at 300 °C, and BiCl₃/SiO₂ was degassed at 100 °C both for 1.5 h under inert gas flow prior analysis. Specific surface area, total pore volume, and pore diameter of samples was obtained by Brunauer–Emmett–Teller (BET) method using BELSORP analysis software. Thermogravimetric analysis (TGA) measurements of silica gel and BiCl₃/SiO₂ were carried out in Perkin–Elmer Pyris Diamond instrument from 32 to 600 °C, using a ramp rate of 10 °C/min under dry N₂.

¹H and ¹³C NMR spectra were recorded on a Bruker-500. All NMR samples were measured in CDCl₃ and chemical shifts are expressed as ppm relative to internal Me₄Si. Mass spectra were obtained on a Fisons instrument. Substrates are commercially available and used without further purification.

2.2. Preparation of BiCl₃/SiO₂ catalyst

30 g of silica gel (300–400 mesh) were activated by refluxing with 150 mL of 6 mol L^{-1} hydrochloric acid under stirring for 24 h, then the activated silica gel was filtered and washed with doubly distilled water to neutral and dried under vacuum at 70 °C for 24 h.

Bismuth(III) chloride (1.575 g, 5 mmol) was added to a suspension of activated silica gel (17.5 g) in toluene (30 mL). The mixture was stirred at room temperature overnight and filtered off. The solid was washed with ethanol and filtered off. The obtained solid was dried at 120 °C under vacuum for 5 h to furnish BiCl₃/SiO₂ as a white free-flowing powder (6.1 wt% of O-BiOCl species as determined by TGA and 5.0 mol% of Bi as determined by Atomic Absorption Spectrophotometry).

2.3. General procedure for the acid-catalyzed Paal–Knorr pyrrole cyclocondensation

Silica-supported bismuth(III) chloride (0.30 g) was well stirred in hexane (5 mL) for a few minutes. Primary amine (1 mmol) and hexane-2,5-dione (1.2 mmol) were then added and the mixture was stirred at room temperature for 1 h. The progress of the reaction was monitored by TLC or GC. Upon the completion of the reaction, the mixture was filtered off and the solid was washed with dichloromethane. The combined organic phase was evaporated under reduced pressure and afforded the crude product. It was passed through a short column of neutral alumina [eluted with ethyl acetate/hexane (1:9)] to give the pure products.

Textural	data	of SiO ₂	and	BiCl ₂	/SiOa
ICALUIUI	uata	01 510)	anu	DICI	1510).

Sample	BET surface area (m²/g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
SiO ₂	493	0.77	63
BiCl ₃ /SiO ₂	372	0.61	65

2.4. Selected spectroscopic data

Although pyrroles **1c** and **1f** are known, no spectroscopic data were found in the literature. All of the products were characterized by ¹H NMR, ¹³C NMR and MS spectral analyses.

2.4.1. N-(4'-Methylphenyl)-2,5-dimethylpyrrole (**1b**) [CAS Registry no. 5044-26-8] [42]

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 15.8 Hz, 2H), 7.24 (d, J = 15.8 Hz, 2H), 6.06 (s, 2H), 2.59 (s, 3H), 2.19 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 137.3, 136.2, 129.5, 127.7, 105.4, 21.0, 12.9; MS (EI), m/z (rel. intensity %) 185 (M⁺, 75), 184 (100), 170 (15), 154 (10), 129 (20), 91 (10), 77 (5).



Fig. 1. TGA plots of (a) BiCl₃, (b) SiO₂ activated, (c) BiCl₃/SiO₂.

Table 2 Types of bismuth moieties on SiO₂.

Bismuth moiety	Support	Weight loss (%)	
		Calculated	Found
BiCl ₃	SiO ₂	8.3	_
BiCl ₂	SiO ₂	7.4	_
BiCl	SiO ₂	6.5	6.1 ^a
Bi	SiO ₂	5.6	5.5 ^b

^a Determined by TGA.

^b Determined by Atomic Absorption Spectrometry.

2.4.2. N-(3'-Methylphenyl)-2,5-dimethylpyrrole (**1c**) [CAS Registry no. 32570-10-8] [48]

¹H NMR (500 MHz, CDCl₃) δ 7.43 (t, *J* = 15.2 Hz, 1H), 7.29 (d, *J* = 15.2 Hz, 1H), 7.12 (s, 1H), 7.11 (s, 1H), 6.00 (s, 2H), 2.50 (s, 3H), 2.14 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 129.7, 129.6, 128.7, 128.6, 128.0, 127.7, 127.5, 105.4, 21.1, 12.9; MS (EI), *m/z* (rel. intensity %) 185 (M⁺, 65), 184 (100), 170 (15), 154 (10), 129 (20), 91 (10), 77 (5).

2.4.3. N-(4'-Nitrophenyl)-2,5-dimethylpyrrole (**1e**) [CAS Registry no. 5044-22-4] [42]

¹H NMR (500 MHz, CDCl₃) δ 8.34 (dd, J = 13 Hz, 2H), 7.39 (d, J = 15 Hz, 2H), 5.95 (s, 2H), 2.06 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 146.7, 144.7, 128.7, 128.5, 124.5, 107.3, 13.1; MS (EI), m/z (rel. intensity %) 217 (30), 216 (M⁺, 100), 215 (70), 169 (40), 154 (50), 77 (15), 30 (40).

2.4.4. N-(3'-Nitrophenyl)-2,5-dimethylpyrrole (**1f**) [CAS Registry no. 32570-23-3]

¹H NMR (500 MHz, CDCl₃) δ 8.30 (m, 1H), 8.12 (s, 1H), 7.69 (t, 1H), 7.60 (t, 1H), 5.95 (s, 2H), 2.08 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 148.6, 140.2, 134.6, 134.1 (2C), 123.2, 123.1, 108.4 (2C), 12.9 (2C); MS (EI), *m*/*z* (rel. intensity %) 217 (20), 216 (M⁺, 100), 215 (80), 199 (10), 169 (20), 154 (20), 77 (15).

3. Results and discussion

3.1. Preparation and characterization of BiCl₃/SiO₂ catalyst

Supported bismuth(III) chloride on silica gel was prepared by adding BiCl₃ to a suspension of activated silica gel (0.29 mmol g^{-1} SiO₂) in toluene at room temperature overnight.

Table 3

Solvent effect on the synthesis of 1a in the presence of BiCl₃/SiO₂.

The physical structure of silica gel (high surface area, large pore volume, etc.) is one of the major reasons for its effectiveness as a support material. However, these features were altered significantly during its chemical modification with bismuth chloride. As shown in Table 1, the Brunauer–Emmett–Teller (BET) method determines the dispersion of the active groups and the diffusion of reagents in the active site of silica gel. The observed reduction in surface area and pore volume of BiCl₃/SiO₂ as compared to silica gel can be attributed to the surface coverage of silica gel by BiCl₃ to define a new modified heterogeneous catalyst.

On the other hand, the thermogravimetric analysis (TGA) gives information on the thermal stability of loaded BiCl₃ on silica gel and whether it is chemically bound to the silica surface.

As shown in Fig. 1, TG curves of 13.9% $BiCl_3/SiO_2$ and 5.4% SiO_2 show a weight loss of around 5.1% and 2.7% up to 130 °C which can be attributed to loss of surface physisorbed water and organic materials. It shows a further weight loss of 8.8% and 2.7% gradually in the range of 130–600 °C for $BiCl_3/SiO_2$ and SiO_2 , respectively. Different from silica gel, the $BiCl_3/SiO_2$ presents an additional 6.1% weight loss, mainly attributed to the loading $BiCl_3$ (Fig. 1b,c).

The bismuth content of BiCl₃/SiO₂ was measured by the atomic absorption spectrometry and found to be 5.5% weight (5 mol%). Moreover, the chloride content of the catalyst was determined by a titration of 0.1 M AgNO₃ solution with K₂CrO₄ as an indicator (Mohr method) to show that 2 chloride ions per BiCl₃ have been released. These supporting evidences are very close to that obtained from TGA data and show that the exact weight loss of BiCl₃/SiO₂ is attributed to the formation of -O-BiOCl species on silica gel (Table 2). The catalyst was washed with ethanol and then separated by simple filtration. The atomic absorption spectroscopy of the filtrate shows the absence of the bismuth, indicating that there is almost no leaching of bismuth from the catalyst.

3.2. Optimization of the model reaction

To evaluate the efficiency of BiCl₃/SiO₂, the reaction of hexane-2,5-dione with aniline at room temperature was carried out. In order to determine the optimum conditions, the solvent effect, the proportions of catalyst to substrate and the reaction time were examined.

The effect of various solvents on the yield of product is given in Table 3. Low and even poor yields of product **1a** were obtained in water, tetrahydrofuran, ethyl acetate, acetonitrile, and



Entry	Solvent	Time (h)	Conversion (%) ^a
1	_	1	93
2	Methanol	1	90
3	Ethanol	1	88
4	Water	1	4
5	Tetrahydrofuran	1	23
6	Ethyl acetate	1	25
7	Acetonitrile	1	11
8	Dichloromethane	1	19
9	Hexane	1	98

^a Gas Chromatography assay (%).

dichloromethane (Table 3, entries 4-8). Both ethanol and methanol as well as solvent-free conditions gave about 90% yield of 1a (Table 3, entries 1-3), whereas hexane was found to be the most effective solvent (Table 3, entry 9).

To investigate the role of BiCl₃/SiO₂, the same reaction was carried out in the absence or presence of catalyst. In the absence of BiCl₃/SiO₂, low yield of product **1a** was obtained, which indicates that catalyst is obviously necessary for the reaction (Table 4. entries 1-2). A remarkable yield for 1a was observed (76%) when the reaction was carried out under catalytic influence of BiCl₃ (Table 4, entry 3), indicating the prominent role of BiCl₃ as Lewis acid catalyst. In contrast, heterogeneous BiCl₃/SiO₂ proved to be more effective compared to BiCl₃ itself (Table 4, entries 4–7). Therefore, the remarkable efficiency of BiCl₃/SiO₂ can be explained by a better synergetic effect of BiCl₃ with SiO₂, due to the existence of multiple Lewis acid catalytic centers.

In the study of catalyst loading, the effect of the relative amounts of BiCl₃/SiO₂ (i.e., active species of BiCl₃) on the outcome of the model reaction was also studied. The optimum amount of BiCl₃/SiO₂ was found to be 0.30 g of catalyst containing 0.075 mmol of BiCl₃ per 1 mmol of substrate (Table 4, entry 6). The fewer amount gave a lower yield, and the more amounts could not cause the obvious increase for the yield of product.

The study on the reaction time showed that BiCl₃/SiO₂ gave 90% yield of product within 15 min. However, the optimal reaction time is 60 min leading to quantitative conversion of 1a (98%).

3.3. Evaluation of the reaction scope

To expand the generality of this novel catalytic method, various aromatic primary amines were tested under the optimized conditions and the results are presented in Table 5. In all cases, the reactions proceeded at room temperature, although the yields were highly dependent on the substrate used. Although the aromatic amines bearing para- and meta-NO₂ are enough active substrates, the ortho-NO₂ isomer shows very poor activity which may be due to the existence of the steric hindered effect (Table 5, 1e-g).

It is noteworthy to mention that the classical reaction for the synthesis of 1g in boiling acetic acid during 7 h gave 23% yield [49], while the same yield was obtained under BiCl₃/SiO₂ catalyzed reaction conditions at ambient temperature within 1 h.

There are recent reports of carrying out this reaction in the presence of other catalysts under heterogeneous conditions. The data presented in Table 6 show the promising features of this protocol in terms of reaction rate, product yield, low catalyst loading, and catalyst reusability when compared with other methods.

The reason why the BiCl₃/SiO₂ is so efficient is not known. The reaction is likely to take place inside the silica-cavities, which hold the bismuth in the appropriate conformation for Lewis acid activation. Bismuth (a heavier p-block element) has potential for both

Table 4			
BiCl ₃ /SiO ₂ catalytic effect	on th	e synthesis	of 1a

Entry	Catalyst amount (g)	Loaded BiCl ₃ (mmol)	Solvent	Time (h)	Conversion (%) ^a
1	_	_	Hexane	1	30
2	0.20 ^b	-	Hexane	1	47
3	-	0.05	Hexane	1	76
4	0.10	0.025	Hexane	1	87
5	0.20	0.05	Hexane	1	95
6	0.30	0.075	Hexane	1	98
7	0.40	0.10	Hexane	1	98

Gas Chromatography assay (%).

^b Activated silica gel in the absence of BiCl₃.

Table 5

Synthesis of N-substituted pyrroles catalyzed by BiCl₂/SiO₂ (7.5 mol%) in hexane within 1 h

Product designation	Product	Conversion (%) ^a	Yield (%) ^b
1a		98	92
1b	Me - N	90	81
1c	Me N	81	73
1d	Me N	53	46
1e		57	50
1f	O ₂ N	81	71
1g		31	22
1h	Br - N	100	96
1i		81	72
1j		100	94
1k	Me Me Me	65	58
11		92	86

^b Yields refer to those of pure isolated products.

Method	Catalyst/Solvent	Temperature	Time	Yield (%)	Catalyst reusability	[Ref]
1	Montorillonite KSF	25 °C	10 h	96	_	[32,33]
2	Montorillonite K10	90 °C ^a	3 min	98	_	[34]
3	Fe ³⁺ -montmorillonite/CH ₂ Cl ₂	25 °C	3 h	96	3 Runs	[36]
4	Zirconium sulfophenyl phosphonate (6 mol%)	60 °C	2 h	88	3 Runs	[37]
5	α-Zirconium potassium phosphate (12 mol%)	60 °C	24 h	56	3 Runs	[37]
6	[Bmim]I ionic liquid	25 °C	3 h	96	3 Runs	[38]
7	Bismuth nitrate (50–100 mol%)/CH ₂ Cl ₂	25 °C	10 h	96	_	[45]
8	BiCl ₃ /SiO ₂ (7.5 mol%)/C ₆ H ₁₄	25 °C	1 h	92	6 Runs	This work

^a Microwave irradiation.



Scheme 2. Plausible mechanism for BiCl₃/SiO₂ catalyzed Paal-Knorr pyrrole cyclocondensation.

covalent and coordinate bonding due to weak shielding of the 4fshell (lanthanide contraction). This lowers the activation energy of the reaction.

Accordingly, we propose a plausible mechanism for the BiCl₃/ SiO₂ catalyzed double condensation of hexane-2,5-dione with primary amine in Scheme 2. Bismuth sites of the catalyst interact with carbonyl groups of the dicarbonyl compound to form the activated carbonyls of complex **A**. Nucleophilic attack of the



Fig. 2. Recyclability of BiCl₃/SiO₂ in hexane for the synthesis of 1a.

primary amine on the activated carbonyls in complex **A** produces the intermediates **B** and **C**. Eventually, detachment of bismuth ion and subsequent loss of water (intermediate **D**) leads to the formation of the pyrrole ring.

3.4. Recycling of BiCl₃/SiO₂

The reusability of catalyst in hexane was also examined. As shown in Fig. 2, the catalyst was recycled for subsequent runs. It was found that the catalyst is still active in hexane even in sixth run without great loss of activity. The recovery of catalyst was very easy. Product is soluble in hexane, while the catalyst remains insoluble. After completion of the reaction, the catalyst was simply filtered from the reaction mixture, washed with dichloromethane, dried at 120 °C for 2 h and reused in subsequent run. No fresh catalyst was added.

4. Conclusion

In conclusion, BiCl₃/SiO₂ is introduced as a novel heterogeneous Lewis acid catalyst for the Paal–Knorr pyrrole cyclocondensation. In most cases, the catalyst showed moderate to excellent activity for the condensation reaction. The procedure offers several advantages including low catalyst loading, operational simplicity, and increased variation of substituents in the product.

The catalyst was stable under the reaction conditions, and its activity in terms of yields slightly decreased with increasing number of cycles of the reaction (conversion: 98% for the first run; 72% for the sixth run) making the procedure a powerful tool from an industrial vantage point.

References

- [1] B.S. Kwak, Catal. Surv. Asia 9 (2005) 103-116.
- [2] M.J. Climent, A. Corma, S. Iborra, Chem. Rev. 111 (2011) 1072-1133.
- [3] A. Corma, Chem. Rev. 95 (1995) 559-614.
- [4] K. Wilson, J.H. Clark, Pure Appl. Chem. 72 (2000) 1313–1319.
- [5] T. Okuhara, Chem. Rev. 102 (2002) 3641-3666.
- [6] J.H. Clark, Acc. Chem. Res. 35 (2002) 791-797.
- [7] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307-4365.
- [8] G. Sartori, R. Ballini, F. Bigi, G. Bosica, R. Maggi, P. Righi, Chem. Rev. 104 (2004) 199–250.
- [9] A. Fürstner, H. Szillat, B. Gabor, R. Mynott, J. Am. Chem. Soc. 120 (1998) 8305–8314.
- [10] P.A. Jacobi, L.D. Coutts, J. Guo, S.I. Hauck, S.H. Leung, J. Org. Chem. 65 (2000) 205–213.
- [11] A. Fürstner, Angew. Chem. Int. Ed. 42 (2003) 3582-3603.
- [12] R.A. Jones, G.P. Bean, The Chemistry of Pyrroles, Academic Press, London and New York, 1977.
- [13] C.Y. de Leon, B. Ganem, Tetrahedron 53 (1997) 7731-7752.
- [14] R. Di Santo, R. Costi, M. Artico, S. Massa, G. Lampis, D. Deidda, R. Pompei, Bioorg. Med. Chem. Lett. 8 (1998) 2931–2936.
- [15] R. Ragno, G.R. Marshall, R. Di Santo, R. Costi, S. Massa, R. Rompei, M. Artico, Bioorg. Med. Chem. 8 (2000) 1423-1432.
- [16] H. Hoffmann, T. Lindel, Synthesis 12 (2003) 1753-1783.
- [17] F. Bellina, R. Rossi, Tetrahedron 62 (2006) 7213-7256.
- [18] C. Haubmann, H. Hübner, P. Gmeiner, Bioorg. Med. Chem. Lett. 9 (1999) 3143-3146.
- [19] J. Robertson, R.J.D. Hatley, D.J. Watkin, J. Chem. Soc. Perkin Trans. 1 (2000) 3389-3396.
- [20] N.R. Wurtz, J.M. Turner, E.E. Baird, P.B. Dervan, Org. Lett. 3 (2001) 1201-1203.
- [21] R.U. Braun, K. Zeitler, T.J.J. Müller, Org. Lett. 3 (2001) 3297–3300.

- [22] V.F. Ferreira, M.C.B.V. De Souza, A.C. Cunha, L.O.R. Pereira, M.L.G. Ferreira, Org. Prep. Proced. Int. 33 (2001) 411-454.
- [23] G. Balme, Angew. Chem. Int. Ed. 43 (2004) 6238-6241.
- [24] U. Joshi, M. Pipelier, S. Naud, D. Dubreuil, Curr. Org. Chem. 9 (2005) 261–288.
 [25] S. Agarwal, S. Cämmerer, S. Filali, W. Fröhner, J. Knöll, M.P. Krahl, K.R. Reddy,
- H.-J. Knölker, Curr. Org. Chem. 9 (2005) 1601–1614. [26] M. Biava, G.C. Porretta, G. Poce, S. Supino, G. Sleiter, Curr. Org. Chem. 11 (2007)
- 1092–1112.
- [27] C. Schmuck, D. Rupprecht, Synthesis 20 (2007) 3095–3110.
 [28] J. Roger, H. Doucet, Adv. Synth. Catal. 351 (2009) 1977–1990.
- [29] G. Minetto, L.F. Raveglia, M. Taddei, Org. Lett. 6 (2004) 389–392.
- [30] B. Tan, Z. Shi, P.J. Chua, Y. Li, G. Zhong, Angew. Chem. Int. Ed. 48 (2009) 758–761.
- [31] R. Ballini, L. Barboni, G. Bosica, M. Petrini, Synlett 3 (2000) 391–393.
- [32] S. Samadiar, F.F. Becker, B.K. Banik, Heterocycles 55 (2001) 1019–1022.
- [33] B.K. Banik, S. Samajdar, I. Banik, J. Org. Chem. 69 (2004) 213–216.
- [34] M. Abid, A. Spaeth, B. Török, Adv. Synth. Catal. 348 (2006) 2191–2196.
- [35] F. Texier-Boullet, B. Klein, J. Hamelin, Synthesis 5 (1986) 409-411.
- [36] G. Song, B. Wang, G. Wang, Y. Kang, T. Yang, L. Yang, Synth. Commun. 35 (2005) 1051–1057.
- [37] M. Curini, F. Montanari, O. Rosati, E. Lioy, R. Margarita, Tetrahedron Lett. 44 (2003) 3923–3925.
- [38] B. Wang, Y. Gu, C. Luo, T. Yang, L. Yang, J. Suo, Tetrahedron Lett. 45 (2004) 3417–3419.
- [39] J. Chen, H. Wu, Z. Zheng, C. Jin, X. Zhang, W. Su, Tetrahedron Lett. 47 (2006) 5383–5387.
- [40] T.N. Danks, Tetrahedron Lett. 40 (1999) 3957–3960.
- [41] Z.-H. Zhang, J.-J. Li, T.-S. Li, Ultrason. Sonochem. 15 (2008) 673-676.
- [42] J.-X. Chen, M.-C. Liu, X.-L. Yang, J.-C. Ding, H.-Y. Wu, J. Braz. Chem. Soc. 19 (2008) 877–883.
- [43] J. Chen, X. Yang, M. Liu, H. Wu, J. Ding, W. Su, Synth. Commun. 39 (2009) 4180–4198.
- [44] J.S. Yadav, B.V.S. Reddy, B. Eeshwaraiah, M.K. Gupta, Tetrahedron Lett. 45 (2004) 5873–5876.
- [45] B.K. Banik, I. Banik, M. Renteria, S.K. Dasgupta, Tetrahedron Lett. 46 (2005) 2643–2645.
- [46] H.R. Darabi, K. Aghapoor, F. Mohsenzadeh, F. Taala, N. Asadollahnejad, A. Badiei, Catal. Lett. 133 (2009) 84–89.
- [47] H.R. Darabi, K. Aghapoor, F. Mohsenzadeh, M.R. Jalali, Sh. Talebian, L. Ebadi-Nia, E. Khatamifar, A. Aghaee, Bull. Korean Chem. Soc. 32 (2011) 213–218.
- [48] M.R. Bell, R. Oesterlin, US Patent 3,928,380 (1975).
- [49] N.V. Subba Rao, K. Sudarsana Rao, Proc. Indian Acad. Sci. Sect. A 73 (1971) 59–63.