Preparation of Silica-bonded Propyl-diethylene-triamine-*N*-sulfamic Acid as a Recyclable Catalyst for Chemoselective Synthesis of 1,1-Diacetates

Nouri Sefat, Maryam Deris, Abdolah Niknam, Khodabakhsh*

Chemistry Department, Faculty of Sciences, Persian Gulf University, Bushehr, 75169, Iran

A simple and efficient procedure for the preparation of silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid (SPDTSA) by reaction of 3-diethylenetriamine-propylsilica (DTPS) and chlorosulfonic acid in chloroform is described. Silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid is employed as a recyclable catalyst for the synthesis of 1,1-diacetates from aromatic aldehydes and acetic anhydride under mild and solvent-free conditions at room temperature. Catalyst could be recycled for several times without any additional treatment.

Keywords silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid, 1,1-diacetates, aromatic aldehydes, catalyst, solvent-free

Introduction

Selective protection and deprotection of carbonyl groups are essential steps in modern organic chemistry.[1] The protection of aldehydes as acetals, acylals, oxathioacetals, or dithioacetals is common practice for manipulation of other functional groups during multi-step syntheses. Protection of aldehydes as acylals is often preferred due to their ease of preparation and their stability towards basic and neutral conditions.[1,2] In addition, the preparation of 1,1-diacetates from the corresponding aldehydes can be achieved very easily in the presence of ketones. Moreover, they also serve as valuable precursors for asymmetric allylic alkylation[3] and natural product synthesis[4] as well as for the synthesis of 1-acetoxydienes and 2,2-dichlorovinylacetates for Diels-Alder reactions.[5,6] Acylals have also been used as cross-linking agents for cellulose in cotton[7] and are useful intermediates in industry.[5] Moreover, the acylal functionality can be converted into other functional groups by reaction with appropriate nucleophiles.[8,9] Generally, they are synthesized from acetic anhydride and aldehydes using strong protonic acids,[6,10,11] Lewis acids,[2,12-14] heterogeneous catalysts,[15,16] and supported reagents.[17,18] Other catalysts, such as iodine,[19] copper *p*-toluene-sulfonate/HOAc,[20] and 1,3-dibromo-5,5-dimethylhydantoin,[21] have also been used for this transformation, but these procedures are often accompanied by longer reaction times, poor product yields, stringent conditions, good catalyst loading; require the use of toxic solvents; and so on. More recently, supported catalysts,[22,23] silica-bonded S-sulfonic acid,[24] poly(*N*,*N'*-dibromo-*N*-ethylbenzene-1,3-disulfonamide),[25] ferrous methansulfonate,[26] cobalt(II) bromide,[27] and SO_3H-functionalized ionic liquids,[28] were reported for the synthesis of 1,1-diacetates.

Heterogenization of homogeneous catalysts has been an interesting area of research from the industrial point of view; this combines the advantages of homogeneous catalysts (high activity and selectivity, *etc.*) with the engineering advantages of heterogeneous catalysts (easy catalyst separation, long catalytic life, easy catalyst regenerability, thermal stability and recyclability).[29]

Several types of solid sulfonic acid functionalized silica (both amorphous and ordered) have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations.[30-36] In continuation of our studies on the design and application of solid acid catalysts in organic transformations,[31-36] herein, we describe the preparation and application of silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid (SPDTSA) as a new and recyclable catalyst for the synthesis of 1,1-diacetates (Scheme 1).

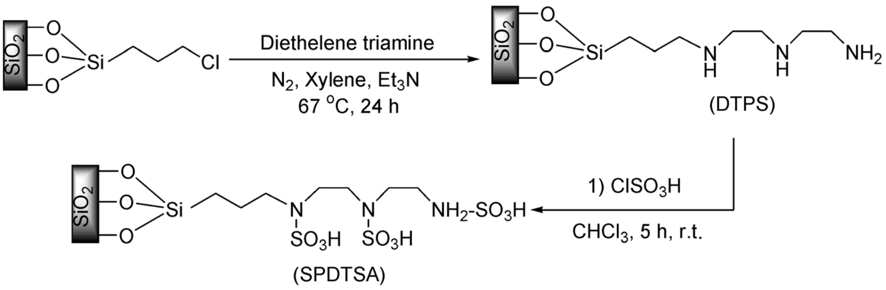
Results and discussion

Silica-bonded propyl-diethylene-triamine-*N*-sulfamic acid (SPDTSA) was prepared by reaction of 3-diethylenetriamine-propylsilica (DTPS) and chlorosulfonic acid in chloroform. The BET surface area analysis using nitrogen adsorption isotherms at the temperature of liquid nitrogen gave the results of $a_{s,BET}$ 762 $m^2 \bullet g^{-1}$ and the total pore volume 0.1342 $cm^3 \bullet g^{-1}$ (see supplementary material). The elemental analysis gave the results: C, H, N, and S content to be 10.3%,

---

* E-mail: khniknam@gmail.com, niknam@pgu.ac.ir; Fax: (＋98) 771-4545188
Received March 3, 2011; revised June 23, 2011; accepted July 19, 2011.

Scheme 1



2.7%, 3.1%, and 3.17% respectively. According to S content typically a loading of 0.99 mmol/g H^+ was obtained. The thermal stability of the catalyst was an important property for the catalyst. TG curve for the catalyst was shown in Figure1. The decrease in gravity began at about 120 ℃ which indicated the decomposition of the catalyst. The covalent chemical bonds connection made the catalyst own high thermal stability.

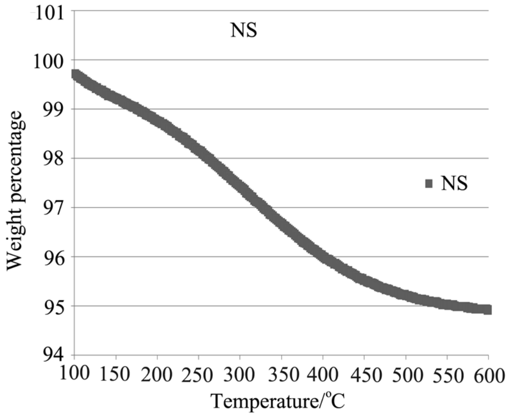


Figure 1 TGA of the SPDTSA.

To study the effect of catalyst loading on the protection of aromatic aldehydes as the corresponding 1,1-diacetates, the reaction of 4-chlorobenzaldehyde with acetic anhydride was chosen as a model reaction (Table 1). The results show clearly SPDTSA are effective catalyst for this transformation and in the absence of SPDTSA the reaction did not take place, even after 12 h. Although lower catalyst loading 0.005 g of SPDTSA accomplished this protection, however, 0.01 g of SPDTSA per 1 mmol of aldehyde was optimum in terms of reaction time and isolated yield. Also, as shown in Table 1, the best result in the case of time and isolated yield was obtained by using 15 mmol of acetic anhydride.

The model reaction was also examined in various solvents as well as under solvent-free conditions in the presence of 0.01 g of SPDTSA with different amounts of acetic anhydride (Table 2).

The yield of the reaction under solvent-free conditions was the highest and the reaction time was shorter. In protic solvents such as water and ethanol this protection reaction proceeded in longer reaction times and with very poor yields, which may be related to the instability of acetic anhydride in protic solvents. Acetic acid was used as solvent and the reaction was accomplished with longer reaction time and lower yield (Entries 6—9). Therefore, we employed the optimized conditions (0.01 g•mmol^{-1} of SPDTSA, 15 mmol of Ac_2O, and solvent-free conditions) for the conversion of various aldehydes into the corresponding acylals (Scheme 2).

Table 1 Conversion of 4-chlorobenzaldehyde to the corresponding diacetate (**1b**) with different amounts of acetic anhydride in the presence of different amounts of SPDTSA under solvent-free conditions at room temperature

Entry	Catalyst loading/g	Ac_2O/mmol	Time/min	Yield[a]/%
1	No catalyst	15	12 h	0
2	0.005	15	10	90
3	0.01	15	5	95
4	0.01	1	5	70
5	0.01	2	5	70
6	0.01	4	5	75
7	0.01	10	5	82
8	0.01	12	5	87
9	0.015	15	5	95
10	0.03	15	5	95

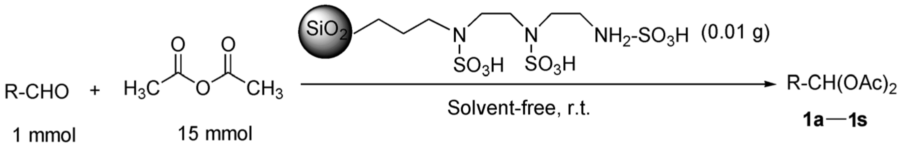
[a] Isolated yield.

Table 2 The reaction of 4-chlorobenzaldehyde (1 mmol) with different amount of Ac_2O in various solvents in the presence of SPDTSA (0.01 g) into the corresponding diacetate (**1b**)

Entry	Solvent[a]	Ac_2O/mmol	Time/min	Yield[b]/%
1	EtOH	1	45	15
2	H_2O	1	45	30
3	CH_2Cl_2	1	5	89
4	*n*-hexane	1	30	84
5	MeCN	1	5	84
6	MeCOOH	1	10	70
7	MeCOOH	2	10	70
8	MeCOOH	4	10	75
9	MeCOOH	10	10	80
10	solvent-free	15	5	95

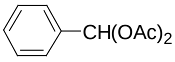
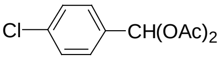
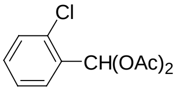
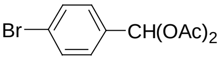
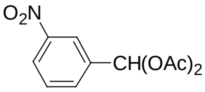
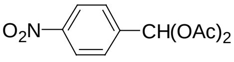
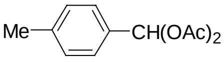
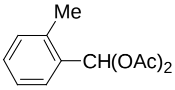
[a] The reaction was carried out in 5 mL of solvent at r.t. [b] Isolated yield.

Scheme 2

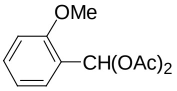
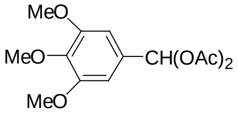
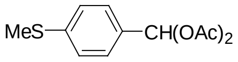
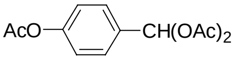
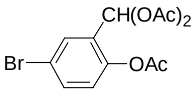
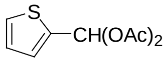
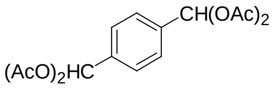
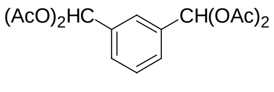
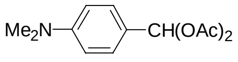
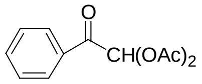
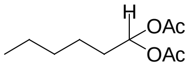
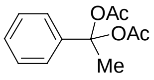
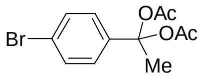


The results of the solvent-free preparation of acylals from aromatic aldehydes in the presence of SPDTSA at room temperature are shown in Table 3. 1,1-Diacetate **1a** was obtained in high yield in 4 min by the reaction of benzaldehyde with acetic anhydride. Benzaldehydes with electron-withdrawing or electron-donating groups, for example, 3-nitro- and 4-nitrobenzaldehyde, or 4-methyl- and 2-methylbenzaldehyde, 2-methoxy- and 3,4,5-trimethoxybenzaldehyde were converted into the corresponding acylals **1e—1j** in high yields after very short reaction times (Table 3, Enties 5—10). The acid-sensitive substrate thiophene-2-carbaldehyde gave the expected acylal **1n** in 81% yield (Table 3, Entry 14). We also investigated the reactions of 4-hydroxybenzaldehyde and 2-hydroxy-5-bromobenzaldehyde under the above-mentioned conditions and observed that both carbonyl and phenolic groups were acylated (Table 3, Entries 12 and 13). Additionally, 4-*N*,*N*-dimethylaminobenzaldehyde failed to give the corresponding 1,1-diacetate and the starting material was quantitatively recovered under the same conditions. The explanation for this result may be due to the strong electron donating dimethylamino group which will reduce the reactivity. A degree of tautomerisation may occur in 4-*N*,*N*-dimethylaminobenzaldehyde with formation of a quininoid structure and thus decrease the reactivity of the aldehyde group (Table 3, Entry 17). 2-Oxo-2-phenylacetaldehyde substrate was exposed to the reaction conditions that only aldehyde group was protected and carbonyl group remained unchanged (Table 3, Entry 18).

Table 3 Reaction of aldehydes with acetic anhydride using SPDTSA as catalyst under solvent-free conditions at room temperature[a]

Entry	Ar	Product	Time/min	Yield[b]/%	M.p./℃
1	C_6H_5-	 **1a**	4	95	44—45 Lit.[18] 45
2	4-Cl-C_6H_4-	 **1b**	5	95	81—83 Lit.[18] 80
3	2-Cl-C_6H_4-	 **1c**	50	90	58—60 Lit.[22] 59
4	4-Br-C_6H_4-	 **1d**	15	80	90—92 Lit.[16] 92—95
5	3-O_2N-C_6H_4-	 **1e**	20	92	64—65 Lit.[24] 65—66
6	4-O_2N-C_6H_4-	 **1f**	4	94	126—128 Lit.[18] 125
7	4-Me-C_6H_4-	 **1g**	4	90	79—81 Lit.[20] 80—82
8	2-Me-C_6H_4-	 **1h**	75	90	63—65 Lit.[21] 75—77

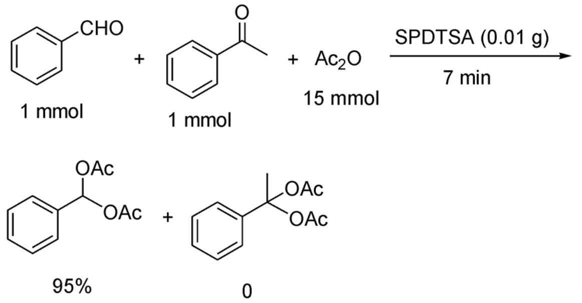
Continued

Entry	Ar	Product	Time/min	Yield^b/%	M.p./℃
9	2-MeO-C_6H_4-	 **1i**	5	60	78—80 Lit.[20] 72—74
10	3,4,5,-$(MeO)_3$-C_6H_2-	 **1j**	4	90	117—119 Lit.[18] 114—116
11	4-MeS-C_6H_4-	 **1k**	90	90	59—61 Lit.[24]
12	4-HO-C_6H_4-	 **1l**	4	60	94—96 Lit.[20] 90—91
13	2-HO,5-Br-C_6H_3-	 **1m**	13	92	94—97
14	2-Thienyl-	 **1n**	25	81	67—68 Lit.[21] 65—67
15	4-OHC-C_6H_4-	 **1o**	5	90	172—174 Lit.[18] 174—175
16	3-OHC-C_6H_4-	 **1p**	3	92	108—110 Lit.[24] 108—110
17	4-$(Me)_2N$-C_6H_4-	 **1q**	24 h	NR	—
18	C_6H_5-CO-	 **1r**	30	94	50—52 Lit.[18] 50—51
19	$Me(CH_2)_4$-	 **1s**	5	68	b.p. 127—129 Lit.[2] b.p. 128—129 (2 mmHg)
20	Acetophenone	 **1t**	2h	NR	—
21	4-Bromoaceto-phenone	 **1u**	2h	NR	—

The aliphatic aldehyde such as hexanal was converted into corresponding acylal in lower yield (Table 3, Entry

19). The protocol was then extended towards the protection of ketones but the reaction did not yield corresponding acylals (Table 3, Entries 20, 21). This prompted us to check and extend the present protocol for chemoselective synthesis of acylals of an aldehyde over ketone. An equimolar (1 mmol each) mixture of benzaldehyde and acetophenone was allowed to react with acetic anhydride (15 mmol) in presence of SPDTSA (0.01 g). However, even after stirring for 7 min at ambient temperature, only benzaldehyde got converted into corresponding acylal leaving acetophenone practically unaffected (Scheme 3).

Scheme 3



Finally, a comparative study of SPDTSA with other recently reported catalysts for acetylation of 4-chlorobenzaldehyde, as a model compound was made which revealed that SPDTSA is an equally efficient but much cheaper and reusable catalyst (Table 4).

Table 4 Comparison of the efficiency of SPDTSA with some of the reported procedure on the reaction of 4-chlorobenzaldelyde with acetic anhydride

Catalyst	Catalyst load/mmol	Time/min	Yield^a/%	Ref.
H_2NSO_3H	0.4	10	92	11
$HClO_4/SiO_2$	0.005	2	98	18
CPTS-HOAc	—^{b}	150	92	20
$H_3PW_{12}O_{40}$-supported MCM-41	0.3 g (20 wt%)	240	91	22
PEG-SO_3H	0.1	30	94	23
$Fe(CH_3SO_3)_2{\bullet}4H_2O$	0.45	360	92	26
$CoBr_2$	0.1	25	93	27
SPDTSA	0.009	5	95	present work

^{a} Isolated yield. ^{b} 0.045 mmol of CPTS and 12 mmol of HOAC were used.

The possibility of recycling the catalyst was examined using the reaction of 4-chlorobenzaldehyde and acetic anhydride under the optimized conditions. Upon completion, the reaction mixture was filtered and the remaining solid was washed with dichloromethane, dried in air and the catalyst reused in the next reaction. The recycled catalyst could be reused six times in the presence of SPDTSA without any additional treatment. No observation of any appreciable loss in the catalytic activity of SPDTSA was observed (Figure 2).

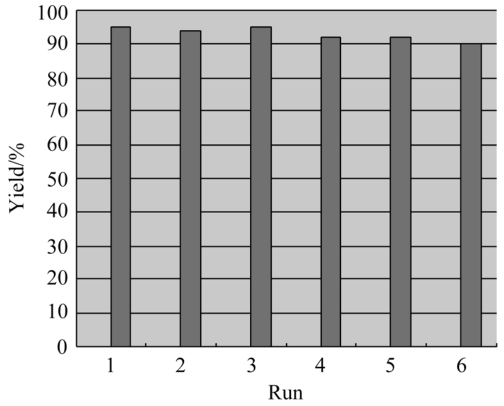


Figure 2 Recyclability of SPDTSA (0.01 g) in the reaction of 4-chlorobenzaldehyde (1 mmol) and acetic anhydride (15 mmol) at room temperature. Reaction time＝5 min.

In conclusion, we have shown that silica-bonded propyl-diethylene-triamine-*N*-sufamic acid (SPDTSA), which can be prepared from commercially available and cheap starting materials, catalyzed efficiently the synthesis of aromatic 1,1-diacetates from aryl aldehydes. The mild reaction conditions, simplicity of the procedure and reusability of catalyst offer improvements over many existing methods.

Experimental section

General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All the products were characterized by comparison of their IR, ^1H NMR and ^{13}C NMR spectroscopic data and their melting points with the reported values.[16-29] Chloropropyl silica was prepared by a known procedure as previously reported.[37]

Preparation of silica propyl chloride

Silica was first immersed in hydrochloric acid for 24 h and then washed with deionized water and dried under vacuum at 120 ℃ for 8 h. The activated silica (25.0 g) was suspended in 300 mL of dry toluene and then an excess of 3-chloropropyltrimethoxysilane (25.0 mL) was added, followed by 2.5 mL of triethylamine (added as a catalyst). The suspension was mechanically stirred and refluxed for 48 h. After refluxing, the reaction was stopped and the modified silica was cooled to room temperature, transferred to a vacuum glass filter, and washed with toluene, ethanol-water mixture, deionized water in turn and finally with methanol. Chloropropyl silica was dried under vacuum at 60 ℃ for 4 h and 28.45 g was obtained.

Preparation of 3-diethylenetriamine-propylsilica (DTPS)

To a mixture of chloropropyl silica (25 g) in anhydrous xylene (250 mL) an excess of diethylenetriamine (25 mL) was added and the mixture was refluxed with stirring for 24 h. After refluxing, the reaction was stopped and the modified silica was cooled to room temperature, transferred to a vacuum glass filter, and washed with xylene and large excess of ethanol in turn. The silica chemically bonded with propyl-diethylenetriamine was dried under vacuum overnight at 80 ℃ and 26.23 g was obtained.

Preparation of silica-bonded propyl-diethylenetriamine-*N*-sufamic acid (SPDTSA)

To a magnetically stirred mixture of 3-diethylenetriamine-propylsilica (DTPS, 5 g) in $CHCl_3$ (20 mL), chlorosulfonic acid (2.00 g, 18 mmol) was added dropwise at 0 ℃ during 2 h. After the addition was complete, the mixture was stirred for 2 h until all HCl was removed from reaction vessel. The mixture was then filtered, washed with methanol (30 mL) and dried at room temperature to give the silica-bonded propyl-diethylenetriamine-*N*-sulfamic acid (SPDTSA) as a white powder (5.39 g). IR, BET, and TGA were running for characterization of SPDTSA (see supplementary materials).

General procedure for the synthesis of 1,1-diacetates

To a mixture of aromatic aldehyde (1 mmol) and acetic anhydride (15 mmol) was added SPDTSA catalyst (0.01 g) and the mixture was stirred at room temperature. When the reaction was complete as judged by TLC, CH_2Cl_2 (5 mL) was added and the reaction mixture was filtered and the remaining solid was washed with CH_2Cl_2 (5 mL×3) in order to separate the catalyst. The CH_2Cl_2 layer was washed with water (10 mL×2) and dried over anhydrous $MgSO_4$. After removal of the solvent *in vacuo*, the obtained residue was recrystallized from ethanol.

Compound 1m (Table 3, Entry 13) ^1H NMR ($CDCl_3$, 500 MHz) δ: 2.13 (s, 6H), 2.35 (s, 3H), 7.04 (d, J=8.6 Hz, 1H), 7.55 (dd, J=8.6, 1.2 Hz, 1H), 7.78 (d, J=2.4 Hz, 1H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.12, 21.23, 84.77, 119.71, 125.40, 130.25, 131.24, 134.12, 147.61, 168.67, 169.45; IR (KBr) ν: 3060, 3015, 2360, 1760, 1490, 1370, 1200, 1120, 1085, 1060, 1000, 970, 945, 840, 745 cm^{-1}. Anal calcd for $C_{13}H_{13}BrO_6$: C 45.24, H 3.80, Br 23.15; found C 45.06, H 3.88.

Compound 1r (Table 3, Entry 18) ^1H NMR ($CDCl_3$, 500 MHz) δ: 2.19 (s, 6H), 7.51 (t, J=7.6 Hz, 2H), 7.63—7.66 (m, 2 H), 7.95 (d, J=7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.01, 86.70, 129.32, 133.62, 134.69, 169.10, 189.23; IR (KBr) ν: 3060, 2955, 1765, 1725, 1710, 1600, 1450, 1380, 1230, 1200, 1050, 1015, 955, 900, 775, 695 cm^{-1}.

Acknowledgment

Financial support for this work by the Research Council of Persian Gulf University, Bushehr, Iran, is gratefully acknowledged. Also, we are thankful to Dr Mohammad Mahdi Doroodmand for helpful comments.

References

1 Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 4th ed., Wiley, New York, **2007**.
2 Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Rajadhyaksha, S. N.; Pinnick, H. W. *J. Org. Chem*. **1983**, *48*, 1765.
3 Trost, B. M.; Lee, C. *J. Am. Chem. Soc*. **2001**, *123*, 12191.
4 Sandberg, M.; Sydnes, L. K. *Org. Lett*. **2000**, *2*, 687.
5 Held, H.; Rengstle, A.; Mayer, D. In *Ullman's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A1, Ed.: Gerhartz, W., Wiley-VCH, New York, **1985**, p. 68.
6 Freeman, F.; Karcherski, E. M. *J. Chem. Eng. Data* **1977**, *22*, 355.
7 Jr Frick, J. G.; Harper, R. J. Jr *J. Appl. Polym. Sci*. **1984**, *29*, 1433.
8 Van Heerden, F. R.; Huyser, J. J.; Bradley, D.; Williams, G.; Holzapfel, C. W. *Tetrahedron Lett*. **1998**, *39*, 5281.
9 Sandberg, M.; Sydnes, L. K. *Tetrahedron Lett*. **1998**, *39*, 6361.
10 Gregory, M. J. *J. Chem. Soc.* (*B*) **1970**, 1201.
11 Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *Green Chem*. **2002**, *4*, 255.
12 Chakraborti, A. K.; Thilagavathi, R.; Kumar, R. *Synthesis* **2004**, 831.
13 Karimi, B.; Maleki, J. *J. Org. Chem*. **2003**, *68*, 4951.
14 Xu, R.; Zhang, J.; Tian, Y.; Zhou, J. *J. Iran. Chem. Soc*. **2009**, *6*, 443.
15 Ballini, R.; Bordoni, M.; Bosica, G.; Maggi, R.; Sartori, G. *Tetrahedron Lett*. **1998**, *39*, 7587.
16 Nagy, N. M.; Jakab, M. A.; Konya, J.; Antus, S. *Appl. Clay Sci*. **2002**, *21*, 213.
17 Heravi, M. M.; Bakhtiari, K.; Bamoharram, F. F. *Catal. Commun*. **2006**, *7*, 499.
18 Khan, A. T.; Choudhury, L. H.; Ghosh, S. *J. Mol. Catal. A*: *Chem*. **2006**, *255*, 230.
19 Deka, N.; Kalita, D. J.; Borah, R.; Sarma, J. C. *J. Org. Chem*. **1997**, *62*, 1563.
20 Wang, M.; Song, Z.; Gong, H.; Jiang, H. *Synth. Commun*. **2008**, *38*, 961.
21 Azarifar, D.; Ghasemnejad, H.; Ramzanian-lehmali, F. *Mendeleev Commun*. **2005**, *15*, 209.
22 Jermy, B. R.; Pandurangan, A. *Catal. Commun*. **2008**, *9*, 577.
23 Wang, Q. Y.; Sheng, S. R.; Wei, M. H.; Xie, Z. L.; Liu, X. L. *Synth. Commun*. **2007**, *37*, 1019.
24 Niknam, K.; Saberi, D.; Nouri Sefat, M. *Tetrahedron Lett*. **2009**, *50*, 4058.
25 Ghorbani-Vaghei, R.; Amiri, M.; Moshfeghifar, N.; Veisi, H.; Dadamahaleh, S. A. *J. Iran. Chem. Soc*. **2009**, *6*, 754.
26 Wang, M.; Tian, G. F.; Song, Z. G.; Jiang, H. *Chin. Chem. Lett*. **2009**, *20*, 1034.
27 Meshram, G. A.; Patil, V. D. *Synth. Commun*. **2010**, *40*,

442.

28 Wang, Y. Y.; Xu, Y. N.; Wang, Z. Z.; Dai, L. Y. *Chin. Chem. Lett*. **2010**, *21*, 524.

29 Li, Z.; Ma, X.; Liu, J.; Feng, X.; Tian, G.; Zhu, A. *J. Mol. Catal. A*: *Chem*. **2007**, *272*, 132.

30 Zareyee, D.; Karimi, B. *Tetrahedron Lett*. **2007**, *48*, 1277.

31 Niknam, K.; Saberi, D. *Tetrahedron Lett*. **2009**, *50*, 5210.

32 Niknam, K.; Saberi, D. *Appl. Catal. A*: *Gen*. **2009**, *366*, 220.

33 Niknam, K.; Saberi, D.; Baghernejad, M. *Chin. Chem. Lett*. **2009**, *20*, 1444.

34 Niknam, K.; Saberi, D.; Molaee, H.; Zolfigol, M. A. *Can. J. Chem*. **2010**, *88*, 164.

35 Niknam, K.; Saberi, D.; Sadegheyan, M.; Deris, A. *Tetrahedron Lett*. **2010**, *51*, 692.

36 Niknam, K.; Mohammadizadeh, M. R.; Mirzaee, S.; Saberi, D. *Chin. J. Chem*. **2010**, *28*, 663.

37 Qiu, H. D.; Jiang, Q.; Wei, Z.; Wang, X. S.; Liu, X.; Jiang, S. X. *J. Chrom. A* **2007**, *1163*, 63.

(E1103033 Cheng, F.)