

Introduction of sulfonated rice husk ash as a highly efficient reusable catalyst for the protection of the hydroxyl group

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ABSTRACT

A mild, efficient and fast method for the trimethylsilyl (TMS), tetrahydropyranyl (THP) and methoxymethyl (MOM) protection of alcohols and phenols in the presence of sulfonated rice husk ash (RHA-SO₃H) is reported. All reactions were performed at room temperature in high to excellent yields. All the products are separated and compared with authentic samples and/ or identified using different types of methods including FT-IR, ¹H NMR and ¹³CNMR spectroscopy. Ease of the preparation and handling of the catalyst, heterogeneous reaction conditions, reusability of the catalyst, easy work-up procedure and short reaction times are the main advantages of this method, which make this procedure useful and attractive addition to the available methods.

Keywords: Sulfonated rice husk ash, Trimethylsilylation, Tetrahydropyranylation, Methoxymethylation, Protection.

1. Introduction

Protection of the hydroxyl group during a multi-step synthetic process as an important method, is attracted the considerable attention of many organic chemists and the selective protection of the hydroxyl group have occupied a unique position in organic synthesis [1]. Between the several methods available for the protection of this functional group, trimethylsilylation, tetrahydropyranylation and methoxymethylation are selected as the most important ones.

Although, appropriate commercially available reagents (such as HMDS, DHP and FDMA) are exist for each type of these protections, but the poor silylating, tetrahydropyranylation and methoxymethylating power of these reagents is considered as the main drawback for the application of these materials.

Several methods have been reported for the preparation of TMS [2-11], THP [12-17] and MOM [18-24] ethers. Although these procedures are useful, most of them suffer from disadvantages such as long reaction times, harsh reaction conditions, use of large amounts of the

catalyst, low selectivity, tedious work-up and use of toxic or expensive reagents. Therefore, introduction of efficient and economical catalysts that solve these drawbacks is desirable.

In recent years, use of green reagents in organic reactions is attracted the attention of many organic chemists. This attention can be attributed to the reduction of environmental pollution and the cost of applied methods.

Rice husk and rice husk ash are two of these types of reagents which are recently used as solid acid catalysts in some of the important organic reactions [25-29].

In the past decade a considerable part of our research program is focused on the development of new methods and use of new reagents for the protection of the hydroxyl groups in organic compounds [17-19, 29-37].

Herein and in continuation of these studies, we wish to report the applicability of sulfonated rice husk ash (RHA-SO₃H) as a newly reported solid acid catalyst [38, 39] in the promotion of the trimethylsilylation, tetrahydropyranylation and methoxymethylation of alcohols and phenols. All reactions are performed under mild reaction conditions in good to high yields.

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2. Experimental

2.1. General procedure

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. All yields refer to the isolated products. All products were characterized by their physical constants and comparison with authentic samples. Also, products were identified using some of different types of spectroscopy methods. The purity determination of the substrate and reaction monitoring were accompanied by thin layer chromatography (TLC) on silica-gel polygram SILG-UV 254 plates.

2.2. Catalyst preparation (RHA-SO₃H)

A 50 mL suction flask charged with 3.0 g of RHA and 10 mL CHCl₃, was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (0.7 mL) and a gas inlet tube for conducting HCl gas into water. Chlorosulfonic acid was added drop wise over a period of 20 min while the reaction mixture was stirred in an ice bath (0 °C). After addition was completed the mixture was stirred for additional 2 h at room temperature. Then, the mixture was filtered and the solid residue washed with methanol (20 mL) and dried at 70 °C for 1 h to afford RHA-SO₃H (3.6 g) as an earthy powder [39]. Also, pH analysis of RHA-SO₃H show that 2.5 mmol H⁺/g are loading on catalyst.

2.3. General procedure for synthesis of trimethylsilyl ethers

A mixture of the substrate (1 mmol), hexamethyl-disilazane (0.70 mmol) and RHA-SO₃H (10 mg, 2.5 mol%) in CH₃CN (3 mL) was stirred at room temperature. The progress of the reaction was monitored by TLC (*n*-hexane: EtOAc; 10:1) and/ or GC. After completion of the reaction, the mixture was filtered to separate the solid catalyst. Then the solution was filtered through a silica gel pad and washed with CH₃CN (2 × 5 mL). Evaporation of the solvent gave the desired products in high purity.

2.4. General procedure for synthesis of tetrahydropyranyl ethers

A mixture of the substrate (1 mmol), 3,4-dihydro-2H-pyran (1.4 mmol) and RHA-SO₃H (5 mg, 1.25 mol%) in CH₂Cl₂ (3 mL) was stirred at room temperature. The reaction was monitored by TLC (*n*-hexane: EtOAc; 10:1) and/ or GC. After completion of the reaction, the mixture was filtered to separate the solid catalyst. Then the solution was filtered through a silica gel pad and washed with CH₂Cl₂ (2×5 mL). Evaporation of the solvent gave the desired products in high purity.

2.5. General Procedure for preparation of methoxymethyl ethers

A mixture of the substrate (1mmol), formaldehydedimethyl-acetal (3 mmol) and RHA-

SO₃H (40 mg, 10 mol%) in CHCl₃ (3 mL) was stirred at reflux temperature. The progress of the reaction was monitored by TLC (*n*-hexane: EtOAc; 10:1) and/ or GC. After completion of the reaction, the solvent was evaporated, and Et₂O (5 mL) was added. The mixture was filtered and the solid residue was washed with Et₂O (5mL). The filtrate was washed with a saturated solution of NaHCO₃ and H₂O and dried over MgSO₄. Evaporation of the solvent afforded the requested MOM ether in high purity.

3. Results and Discussion

Initially the optimization of the reaction conditions was studied with investigating the effect of different molar ratios of the reactants and different solvents and also solvent-free conditions on the reaction of benzyl alcohol and HMDS in terms of time and the product yield.

The best result was obtained by using 10 mg of the catalyst (2.5 mol%) and 0.70 mmol of HMDS in CH₃CN at room temperature (Table 1, entry 4).

After optimization of the reaction conditions and in order to show the general applicability of this method, different types of alcohols were subjected to the same reaction under the determined conditions. The results are summarized in Table 2.

Different types of aromatic and aliphatic alcohols were silylated with HMDS in the presence of a catalytic amounts of RHA-SO₃H in high to excellent yields (Table 2, entries 1-21). This method was found to be useful for the protection of hindered secondary and tertiary alcohols (Table 2, entries 22, 23). Our investigations also showed that under the same reaction conditions RHA-SO₃H is able to catalyze the silylation of phenols in high to excellent yields (Table 2, entries 26-32). In addition, the results show that selective silylation of the hydroxyl group in the presence of NH functional group can be carried out successfully (Table 2, entry 24).

After the successful silylation of alcohols and phenoles, we were interested in extending the applicability of RHA-SO₃H in the preparation of tetrahydropyranyl ethers.

Our investigations clarified that using this method the best results can be obtained when the reaction was proceeded in CH₂Cl₂ using lower amounts of the catalyst (5 mg, 1.25 mol%). The selected conditions are shown in Scheme 1.

After optimization of the reaction conditions different types of benzylic and aliphatic alcohols were subjected to tetrahydropyranylation using DHP in the presence of a catalytic amount of RHA-SO₃H and the results are summarized in Table 3.

Table 1. Reaction of 4-chlorobenzyl alcohol with HMDS in different conditions.

Entry	Catalyst (mg)	HMDS(mmol)	Solvent	Time (min) ^a	Conversion (%) ^b
1	5 (1.25 mol%)	1	CH ₃ CN	3	90
2	10 (2.5 mol%)	1	CH ₃ CN	Immediately	100
3	5	0.7	CH ₃ CN	5	90
4	10	0.7	CH ₃ CN	Immediately	100
5	20 (5 mol%)	0.7	CH ₃ CN	Immediately	100
6	10	0.7	CH ₂ Cl ₂	30	0
7	10	0.7	Solvent-free	6	90

^aImmediately means < 30 sec.^bGC.**Table 2.** Protection of alcohols and phenols by formation of trimethylsilyl ethers catalyzed by RHA-SO₃H.

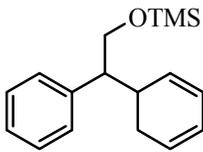
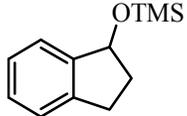
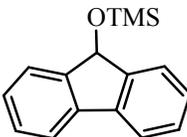
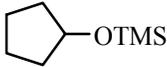
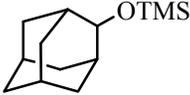
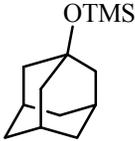
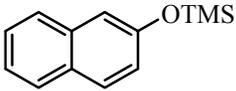
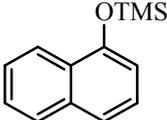
Entry	Product	Time (min) ^a	Yield (%) ^{b,c}
1	C ₆ H ₅ CH ₂ OTMS	Immediately	98, 93 ^d
2	2-ClC ₆ H ₄ CH ₂ OTMS	Immediately	98
3	4-ClC ₆ H ₄ CH ₂ OTMS	Immediately	98
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OTMS	Immediately	98
5	2-BrC ₆ H ₄ CH ₂ OTMS	Immediately	97
6	2-MeC ₆ H ₄ CH ₂ OTMS	Immediately	96
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OTMS	Immediately	97
8	2-OHC ₆ H ₄ CH ₂ OTMS	8	98
9	3-MeOC ₆ H ₄ CH ₂ OTMS	Immediately	97
10	4-MeOC ₆ H ₄ CH ₂ OTMS	Immediately	96
11	2-NO ₂ C ₆ H ₄ CH ₂ OTMS	3	98
12	4-NO ₂ C ₆ H ₄ CH ₂ OTMS	10	98
13	Ph ₂ CHOTMS	Immediately	96
14	PhCH(Me)CH ₂ OTMS	Immediately	98
15		2	97
16		Immediately	97
17		2	98
18	C ₆ H ₅ CH=CHCH ₂ OTMS	2	98

Table 2. (Continued).

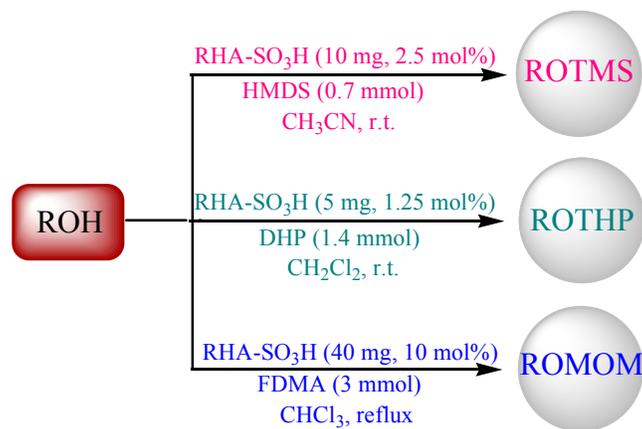
19	$C_6H_5CH_2CH_2OTMS$	Immediately	96
20	$C_6H_5CH_2CH_2CH_2OTMS$	Immediately	97
21		8	97
22		Immediately	97
23		2	96
24	$C_6H_5CH_2NHCH_2CH_2OTMS$	2	98
25	$C_6H_5CH(OTMS)CH_2OTMS$	2	98
26	2-ClC ₆ H ₄ OTMS	4	97
27	4-(Me) ₂ CHC ₆ H ₄ OTMS	Immediately	97
28	4-MeCHC ₆ H ₄ OTMS	2	96
29	3,5-(Me) ₂ C ₆ H ₃ OTMS	Immediately	96
30	2,4-(Me) ₂ C ₆ H ₃ OTMS	2	98
31		Immediately	97
32		Immediately	98

^aImmediately means < 30 sec.

^bIsolated yields.

^cAll products are liquid or oil.

^dYield after seven time.



Scheme 1. Protection of alcohols and phenols in the presence of RHA-SO₃H.

Table 3. Protection of alcohols and phenols by formation of tetrahydropyranyl ethers catalyzed by RHA-SO₃H.

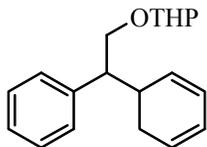
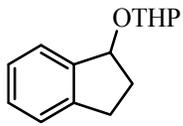
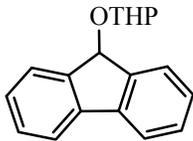
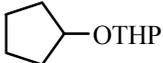
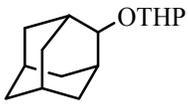
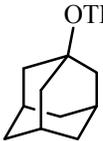
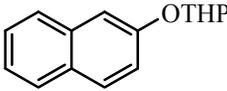
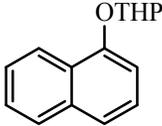
Entry	Product	Time (min) ^a	Yield (%) ^{b,c}
1	C ₆ H ₅ CH ₂ OTHP	2	98, 92 ^d
2	2-ClC ₆ H ₄ CH ₂ OTHP	Immediately	98
3	4-ClC ₆ H ₄ CH ₂ OTHP	Immediately	97
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OTHP	Immediately	98
5	2-BrC ₆ H ₄ CH ₂ OTHP	Immediately	97
6	2-MeC ₆ H ₄ CH ₂ OTHP	2	98
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OTHP	Immediately	98
8	2-OHC ₆ H ₄ CH ₂ OTHP	2	98
9	3-MeOC ₆ H ₄ CH ₂ OTHP	Immediately	96
10	4-MeOC ₆ H ₄ CH ₂ OTHP	Immediately	98
11	2-NO ₂ C ₆ H ₄ CH ₂ OTHP	Immediately	98
12	4-NO ₂ C ₆ H ₄ CH ₂ OTHP	2	97
13	Ph ₂ CHOTHP	2	97
14	PhCH(Me)CH ₂ OTHP	Immediately	97
15		2	98
16		Immediately	98
17		2	96
18	C ₆ H ₅ CH=CHCH ₂ OTHP	Immediately	98
19	C ₆ H ₅ CH ₂ CH ₂ OTHP	Immediately	97
20	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OTHP	Immediately	97
21		Immediately	98
22		2	98
23		2	98
24	C ₆ H ₅ CH ₂ NHCH ₂ CH ₂ OTHP	2	97
25	C ₆ H ₅ CH(OTHP)CH ₂ OTHP	3	96

Table 3. (Continued).

26	2-ClC ₆ H ₄ OTHP	Immediately	96
27	4-(Me) ₂ CHC ₆ H ₄ OTHP	Immediately	97
28	4-MeCHC ₆ H ₄ OTHP	Immediately	98
29	3,5-(Me) ₂ C ₆ H ₃ OTHP	Immediately	98
30	2,4-(Me) ₂ C ₆ H ₃ OTHP	2	97
31		Immediately	98
32		Immediately	98

^aImmediately means < 30 sec.^bIsolated yields.^cAll products are liquid or oil.^dYield after seven time.

Using this method all of the products are obtained in high to excellent yields during acceptable reaction times (Table 3, entries 1-21). Our investigations also showed that under the same reaction conditions RHA-SO₃H is able to catalyze the tetrahydropyranylation of phenols in high to excellent yields (Table 3, entries 26-32).

Finally, we decided to explore the synthesis of methoxymethyl ethers using RHA-SO₃H as the catalyst.

The model reaction was carried out using different solvents (CH₂Cl₂, *n*-hexane, MeOH and CH₃CN) at different temperatures in the presence of various amounts of RHA-SO₃H. The best results were obtained

when 40 mg of RHA-SO₃H (10 mol%) was used in CHCl₃ under reflux conditions (Scheme 1).

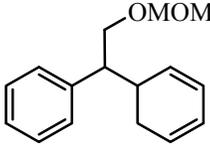
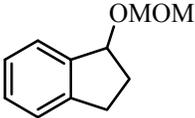
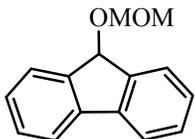
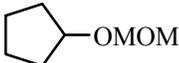
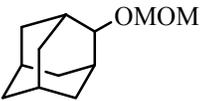
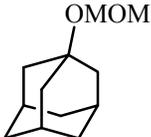
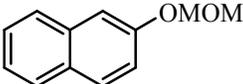
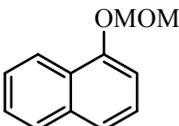
It is clear that all of the reactions proceeded efficiently under the optimized conditions and the corresponding products were obtained in high yields over acceptable reaction time (Table 4).

In continue, we decided to study the catalytic activity of the recycled catalyst for the synthesis of silyl, tetrahydropyranl and methoxymethyl ethers. We found that RHA-SO₃H was a very stable catalyst and could be recycled by filtration, washing with acetone and drying at 70 °C. For the reaction of benzyl alcohol with HMDS, DHP and FDMA even after seven cycles, the catalyst still had excellent activity.

Table 4. Protection of alcohols and phenols by formation of methoxymethyl ethers catalyzed by RHA-SO₃H.

Entry	Product	Time (min)	Yield (%) ^a
1	C ₆ H ₅ CH ₂ OMOM	10	98, 90 ^{b,c}
2	2-ClC ₆ H ₄ CH ₂ OMOM	5	98
3	4-ClC ₆ H ₄ CH ₂ OMOM	10	98
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OMOM	10	97
5	2-BrC ₆ H ₄ CH ₂ OMOM	4	97
6	2-MeC ₆ H ₄ CH ₂ OMOM	5	98
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OMOM	12	98
8	2-OHC ₆ H ₄ CH ₂ OMOM	10	98
9	3-MeOC ₆ H ₄ CH ₂ OMOM	10	98
10	4-MeOC ₆ H ₄ CH ₂ OMOM	8	97
11	2-NO ₂ C ₆ H ₄ CH ₂ OMOM	8	97

Table 4. (Continued).

12	4-NO ₂ C ₆ H ₄ CH ₂ OMOM	10	96
13	Ph ₂ CHOMOM	15	95
14	PhCH(Me)CH ₂ OMOM	5	97
15		18	98
16		25	98
17		25	98
18	C ₆ H ₅ CH=CHCH ₂ OMOM	10	98
19	C ₆ H ₅ CH ₂ CH ₂ OMOM	13	98
20	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OMOM	7	97
21		20	95
22		20	96
23		30	98
24	C ₆ H ₅ CH ₂ NHCH ₂ CH ₂ OMOM	15	98
25	C ₆ H ₅ CH(OMOM)CH ₂ OMOM	35	95
26	2-ClC ₆ H ₄ OMOM	10	98
27	4-(Me) ₂ CHC ₆ H ₄ OMOM	10	98
28	4-MeCHC ₆ H ₄ OMOM	12	97
29	3,5-(Me) ₂ C ₆ H ₃ OMOM	13	98
30	2,4-(Me) ₂ C ₆ H ₃ OMOM	15	98
31		15	96
32		15	96

^aIsolated yields.^bYield after seven time.^cAll products are liquid or oil.

In order to show the efficiency of this method, we compared our results obtained from the silylation, tetrahydropyranylation and methoxymethylation of alcohols with other results reported in the literature (Tables 5). The results indicated that RHA-SO₃H was a very efficient catalyst for this reaction. It is interesting to note that, to compare the applicability and efficiency of RHA-SO₃H with the other catalysts, we also tabulated the TOF (Turnover Frequency) of these catalysts in Table 5. As it is clear RHA-SO₃H is also superior in terms of TOF to the compared catalysts.

4. Conclusions

In conclusion, we have introduced RHA-SO₃H as a highly efficient reusable catalyst for the promotion of the silylation, tetrahydropyranylation and methoxymethylation of alcohols and phenols under mild conditions. Ease of the preparation and handling of the catalyst, simple procedure and easy work-up, short reaction times, excellent yields of the products and reusability of the catalyst are among the other advantages of this method, which make this procedure useful and attractive.

Table 5. Comparison of the results of the silylation, tetrahydropyranylation and methoxymethylation of alcohols catalyzed by RHA-SO₃H with those obtained by some of the reported catalysts.

Entry	Product	Catalyst (mol %)	Time (h)	Yield (%)	TOF(h ⁻¹)	Ref.
1		SiO ₂ -Cl (50 mg)	0.33	98	-	[2]
2		Ti ^{IV} (salophen)(OTf) ₂ (1)	0.01666	100	6000	[3]
3		SANM (7.65)	0.0833	95	149.1	[30]
4	PhCH ₂ OTMS	[Sn ^{IV} (TNH ₂ PP)(OTf) ₂]@CMP (1)	0.0333	100	3003	[4]
5		[Sn ^{IV} (TPP)(BF ₄) ₂] (1)	0.01666	100	6000	[5]
6		[Dsim]HSO ₄ (2)	0.0166	98	2951	[31]
7		Rice husk (80 mg)	0.083	94	-	[29]
8		RHA-SO ₃ H (2.5)	0.0055	100	7272	This work
9		PS/GaCl ₃ (10)	0.333	97	29	[12]
10		[Sn ^{IV} (TNH ₂ PP)(OTf) ₂]@CMP (1)	0.066	95	1439	[13]
11		[V ^{IV} (TPP)(OTf) ₂] (1)	0.033	93	2818	[14]
12	4-OMePhCH ₂ OTHP	Solid silica-based sulfonic acid (2)	0.583	85	73	[15]
13		Silica sulfuric acid (3.9)	0.583	91	40	[16]
14		SANM (3.06)	0.083	98	385	[17]
15		RHA-SO ₃ H (1.25)	0.0055	100	14545	This work
16		SANM (1.15)	2	92	40	[18]
17		MTSA (10)	0.58	92	0.344	[19]
18	PhCH ₂ OMOM	Silica sulfuric acid (52)	1.5	85	1.089	[20]
19		Sn ^{IV} (TPP)(OTf) ₂ (1)	0.166	95	572	[21]
20		Al(HSO ₄) ₃ (20)	1.67	83	2.48	[22]
21		RHA-SO ₃ H (10)	0.166	100	60	This work

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References

- [1] L.F. Fieser, M. Fieser, Reagents for organic synthesis, John Wiley and Sons, New York (1999).
- [2] A. Ziyaei-Halimjani, M.R. Saidi, J. Sci. Islamic Rep. Iran. 17 (2006) 123-126.
- [3] M. Yadegari, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, Polyhedron 31 (2012) 332-338.
- [4] S. Gharaati, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, Polyhedron 35 (2012) 87-95.
- [5] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, S. Gharaati, Polyhedron 29 (2010) 212-219.
- [6] S.T. Kadam, S.S. Kim, J. Organomet. Chem. 694 (2009) 2562-2566.
- [7] H. Firouzabadi, N. Iranpoor, S. Farahi, J. Organomet. Chem. 694 (2009) 3923-3928.
- [8] G. Rajagopal, H. Lee, S.S. Kim, Tetrahedron 65 (2009) 4735-4741.
- [9] B. Karmakar, J. Banerji, Tetrahedron Lett. 51 (2010) 3855-3858.
- [10] H. Firouzabadi, N. Iranpoor, S. Farahi, Catal. Commun. 10 (2009) 1547-1550.
- [11] P. Karthikeyan, S. Arunrao Aswar, P. Narayan Muskawar, P. Rambhau Bhagat, S.S. Kumar, Catal. Commun. 26 (2012) 189-193.
- [12] A. Rahmatpour, Polyhedron 44 (2012) 66-71.
- [13] M. Moghadam, S. Tangestaninejad, V. Mirkhania, I. Mohammadpoor-Baltork, S. Gharaati, J. Mol. Catal. A: Chem. 337 (2011) 95-101.
- [14] S. Abdolmanaf Taghavi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A. R. Khosropour, C. R. Chim. 14 (2011) 1095-1102.
- [15] B. Karimi, M. Khalkhali, J. Mol. Catal. A: Chem. 232 (2005) 113-117.
- [16] D.M. Pore, U.V. Desai, R.B. Mane, B.B. Wadgaonkar, Synth. Commun. 34 (2004) 2135-2142.
- [17] F. Shirini, M. Abedini, A. Nasiri Abkenar, B. Baghernejad, J. Nanostruct. Chem. 4 (2014) 1-6.
- [18] F. Shirini, M. Mamaghani, S. V. Atghia, J. Nanostruct. Chem. 3 (2012) 1-5.
- [19] F. Shirini, M.A. Zolfigol, M. Albadi, Synth. Commun. 40 (2010) 910-914.
- [20] K. Niknam, M. A. Zolfigol, A. Khorramabadi-Zad, R. Zare, M. Shayegh, Catal. Commun. 7 (2006) 494-498.
- [21] S. Gharaati, M. Moghadam, Tangestaninejad, S. Mirkhani, V. Mohammadpoor-Baltork, I. Kosari, F. Inorg. Chim. Acta 363 (2010) 1995-2000.
- [22] K. Niknam, M.A. Zolfigo, M. Shayegh, R. Zare, J. Chinese Chem. Soc. 54 (2007) 1067-1073.
- [23] F. Shirini, G.H. Imanzadeh, S.A.R. Mousazadeh, I. Mohammadpoor-Baltork, M. Abedini, Chinese Chem. Lett. 21 (2010) 1187-1190.
- [24] I. Mohammadpoor-Baltork, M.S. Moghadam, V. Tangestaninejad, M. Mirkhani, A.R. Khosropour, A. Mirjafari, C. R. Chim. 14 (2011) 568-579.
- [25] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, J. Mol. Catal. A: Chem. 363-364 (2012) 10-17.
- [26] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, A. R. Aliakbar, C. R. Chim. 16 (2013) 207-216.
- [27] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, A. R. Aliakbar, C. R. Chim. 16 (2013) 945-955.
- [28] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, Chinese J. Catal. 34 (2013) 2200-2208.
- [29] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, A.R. Aliakbar, C.R. Chim. 17 (2013) 167-170.
- [30] F. Shirini, M. Mamaghani, S.V. Atghia, Appl. Clay Sci. 58 (2012) 67-72.
- [31] F. Shirini, N.G. Khaligh, S. Akbari-Dadamahaleh, J. Mol. Catal. A: Chem. 365 (2012) 15-23.
- [32] F. Shirini, M. Alipour Khoshdel, M. Abedini, S.V. Atghia, Chinese Chem. Lett. 22 (2011) 1211-1214.
- [33] F. Shirini, S. V. Atghia, M. Ghazi Jirdehi, Catal. Commun. 18 (2012) 5-10.
- [34] F. Shirini, M.A. Zolfigol, A. Abri, Monatsh. Chem. 139 (2008) 17-22.
- [35] F. Shirini, M. Abedini, J. Iran. Chem. Soc. 5 (2008) S87-S90.
- [36] F. Shirini, M.A. Zolfigol, M. Abedini, Monatsh. Chem. 140 (2009) 61-64.
- [37] F. Shirini, M.A. Zolfigol, M. Abedini, A.R. Sakhaei, J. Chinese Chem. Soc. 55 (2008) 943-946.
- [38] F. Shirini, M. Mamaghani, M. Seddighi, Catal. Commun. 36 (2013) 31-37.
- [39] M. Seddighi, F. Shirini, M. Mamaghani, RSC Adv. 3 (2013) 24046-24053.