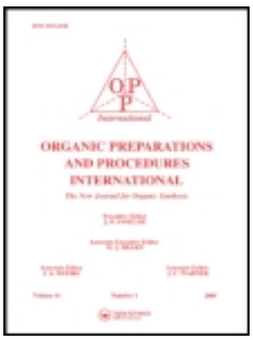


Taylor & Francis
Taylor & Francis Group

Organic Preparations and Procedures International

The New Journal for Organic Synthesis

ISSN: 0030-4948 (Print) 1945-5453 (Online) Journal homepage: http://www.tandfonline.com/loi/uopp20

Synthesis of Pyranopyrazoles using a Magnetically Separable Modified Preyssler Heteropoly Acid

Ali Javid, Amir Khojastehnezhad, Hossein Eshghi, Farid Moeinpour, Fatemeh F. Bamoharram & Javad Ebrahimi

To cite this article: Ali Javid, Amir Khojastehnezhad, Hossein Eshghi, Farid Moeinpour, Fatemeh F. Bamoharram & Javad Ebrahimi (2016) Synthesis of Pyranopyrazoles using a Magnetically Separable Modified Preyssler Heteropoly Acid, Organic Preparations and Procedures International, 48:5, 377-384, DOI: 10.1080/00304948.2016.1206424

To link to this article: http://dx.doi.org/10.1080/00304948.2016.1206424

Organic Preparations and Procedures International, 48:377–384, 2016

ISSN: 0030-4948 print / 1945-5453 online
DOI: 10.1080/00304948.2016.1206424

Synthesis of Pyranopyrazoles using a Magnetically Separable Modified Preyssler Heteropoly Acid

Ali Javid,[1] Amir Khojastehnezhad,[2] Hossein Eshghi,[3] Farid Moeinpour,[4] Fatemeh F. Bamoharram,[5] and Javad Ebrahimi[2]

[1]Department of Chemistry, College of Science, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran
[2]Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran
[3]Department of Chemistry, Faculty of Sciences, Islamic Azad University of Ahvaz and Mashhad, Mashhad, Iran
[4]Department of Chemistry, College of Sciences, Bandar Abbas Branch, Islamic Azad University, Bandar Abbas 7915893144, Iran
[5]Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

The design and preparation of recyclable catalysts are of great economic and environmental importance in the chemical and medicinal industries. Immobilization of homogeneous catalysts on various insoluble supports can lead to simplified catalyst recycling by filtration or centrifugation.[1] Nanoparticles (NPs) are attractive candidates as solid supports for the immobilization of homogeneous catalysts[2] and because of their large surface area, which can bear a large amount of catalytically active species, these supported catalysts display very high activity under mild conditions. Among these NPs, much attention has been directed toward the production of magnetic nanoparticles (MNPs),[3–5] because these NPs can be well dispersed in reaction mixtures without magnetic field thus providing large surface for ready access to substrate molecules. More importantly, after completion of the reactions, the MNP catalysts may be isolated efficiently from the reaction mixture through a simple magnetic separation process.[6,7]

Preyssler heteropoly acid (HPA, $H_{14}NaP_5W_{30}O_{120}$) is an important acid catalyst because it is safe and has significant other advantages such as the availability of fourteen acidic hydro-gens, high thermal stability and high hydrolytic stability (pH 0–12).[8,9] Because their low surface area (7–10 m^2/g) and high solubility in polar solvents, it usually preferable to use them in a supported form such as on acid-neutral solids, such as silica and alumina, activated carbons, zeolites, acidic ion-exchange resins.[8–10]

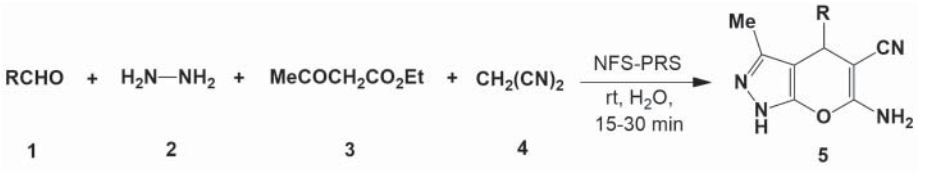
Multi-component reactions (MCRs) have emerged as an efficient and powerful method in modern organic chemistry because the synthesis of complex organic molecules

Received March 12, 2016; in final form June 12, 2016.
Address correspondence to Amir Khojastehnezhad, Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran. E-mail: Akhojastehnezhad@yahoo.com

from simple and readily available substrates can be achieved in a very rapidly and in an efficient manner without the isolation of intermediates.[11–14] MCRs contribute to the principles of an environmentally friendly process by reducing the number of steps, energy consumption and production of waste. Therefore, the discovery for new MCRs and improvement of previously known MCRs with recyclable catalysts are of considerable interest.[15–17]

Pyranopyrazoles constitute an emerging class of heterocycles,[18,19] which is extensively explored as an important core for emerging drugs that display numerous biological properties including potential inhibitor of human Chk1 kinase,[20] anti-inflammatory,[21] anti-cancer, analgesic, molluscicidal[22–24] and antimicrobial activity.[25] Therefore, considerable efforts have been expended to explore new simple and direct approaches towards the construction of the pyranopyrazole skeleton. Most of these methods employ various catalysts such as Fe_3O_4 NPs,[26] β-cyclodextrin,[27] L-proline,[28] acidic ionic liquid,[29] tetra (*n*-butyl)ammonium bromide,[30] P_2O_5-SiO_2,[31] $CeCl_3$ [32] and $NH_4H_2PO_4/Al_2O_3$.[33] Though these catalysts are quite useful, most of them have limitations, such as cost, long reaction times, use of toxic organic solvents and of harsh reaction conditions. Thus, the development of simple, efficient, clean and environ-mentally friendly catalysts for the preparation of these compounds in high yields is an im-portant goal. In continuation of our previous studies,[34–42] the present article describes the results of an investigation of the activity of the Preyssler HPA supported onto the silica coated $NiFe_2O_4$ MNPs (*$NiFe_2O_4$@SiO_2-Preyssler*, abbreviated ***NFS-PRS***) as an efficient and green catalyst for the synthesis of pyranopyrazole derivatives.

To the best of our knowledge, there are no examples of the use of NFS-PRS as a catalyst for the preparation of pyranopyrazoles from the condensation of aromatic aldehydes, hydrazine hydrate, ethyl acetoacetate and malononitrile at room temperature in water. (*Scheme 1*).



a) R = C_6H_5; **b)** R = 4-Cl-C_6H_4; **c)** R = 4-CH_3- C_6H_4; **d)** R = 4-CH_3O-C_6H_4; **e)** 4-Br-C_6H_4; **f)** R = 4-NO2-C_6H_4; **g)** R = 4-F-C_6H_4; **h)** 4-OH-C_6H_4; **i)** 2-CH_3O-C_6H_4; **j)** R = 2-Cl-C_6H_4; **k)** R = 2-NO_2-C_6H_4; **l)** R = 3-Br-C_6H_4; **m)** 3-NO_2-C_6H_4; **n)** R= 3-Cl-C_6H_4; **o)** R = 3-CH_3-C_6H_4

Scheme 1

In order to explore the catalytic activity of catalyst (NFS-PRS), prepared according to our previous work,[43] the four-component reaction of benzaldehyde, hydrazine hydrate, ethyl acetoacetate and malononitrile was carried out as a model reaction. Solvent-free conditions as well as the use of various solvents such as CH_2Cl_2, EtOH, MeOH and H_2O (*Table 1*) were investigated; no product was obtained in the absence of the catalyst (*Entry 1*). The yields of the reaction were better in polar solvents than in non-polar solvents and under solvent-free conditions. It is possible that polar solvents facilitates the dissociation of the HPAs and generate protons; the formation hydrogen-bond between the HPAs and the solvent may also assist the process (*Entries 5–7*).[44] Water gave the best results from among (*Entry 7*). Increasing the reaction time and temperature did not improve the yields

Table 1
Comparison of Different Solvents and Catalysts for the Synthesis of Pyranopyrazole **5a**

Entry	Catalyst	Solvent	Time (min)	Temperature	Yield (%)
1	None	H_2O	120	rt	No reaction
2	NFS-PRS	solvent-free	15	rt	48
3	NFS-PRS	solvent-free	15	100	56
4	NFS-PRS	CH_2Cl_2	15	rt	Trace
5	NFS-PRS	CH_3OH	15	rt	70
6	NFS-PRS	C_2H_5OH	15	rt	83
7	NFS-PRS	H_2O	15	rt	98
8	NFS-PRS	H_2O	15	ref	98
9	NFS-PRS	H_2O	60	ref	97
10	$H_{14}[NaP_5W_{30}O_{110}]$	H_2O	15	rt	90
11	$H_3[PW_{12}O_{40}]$	H_2O	15	rt	82
12	$H_4[SiW_{12}O_{40}]$	H_2O	15	rt	79

(*Entries 8 and 9*). In addition, the model reaction carried out in presence of Preyssler and others HPAs with Keggin structures ($H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$)[45] the same time and conditions led to lower yields than with NFS-PRS as a catalyst (*Entries 10–12*).

In order to determine the optimum quantity of NFS-PRS to be used, the model reaction was carried out under the previously mentioned conditions using different amounts of catalyst (*Table 2*). As already been mentioned, no product was obtained in the absence of the catalyst (*Entry 1*). Increasing the amount of the catalyst improved the yield of **5a** (*Entries 2–5*), with the use of 0.03 g of catalyst resulted in the highest yield in 15 min (*Entry 5*). Further increase of the amount of the catalyst failed to affect the yield noticeably (*Entries 6 and 7*).

The optimized conditions having been determined, the scope and efficiency of the reaction were investigated for the preparation of a variety of substituted 6-amino-4-aryl-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitriles in the presence of NFS-PRS using a number aromatic aldehydes bearing both electron-donating and electron-withdrawing substi-tutents. Excellent yields were obtained as illustrated in *Table 3*.

After the completion of the model reaction, the nano-magnetic catalyst was separated from the reaction mixture by placing an external magnet and decantation of the solution

Table 2
Comparison of the Amount of NFS-PRS and Yields for the Synthesis of Pyranopyrazole **5a**

Entry	Conditions	Catalyst amount (g)	Time (min)	Yield (%)
1	Room temperature/ H_2O	None	120	None
2	Room temperature/ H_2O	0.003	30	39
3	Room temperature/ H_2O	0.007	20	70
4	Room temperature/ H_2O	0.015	15	84
5	Room temperature/ H_2O	0.030	15	98
6	Room temperature/ H_2O	0.050	15	97
7	Room temperature/ H_2O	0.100	15	98

Table 3
Synthesis of Pyranopyrazole (**5a-o**) using of NFS-PRS as Catalyst[a]

Entry	Product	Time (min)	Yield (%)	Found Mp (°C)	Lit. Mp (°C)
1	**5a**	15	98	238–240	244–246[46]
2	**5b**	15	97	233–234	234–236[46]
3	**5c**	20	95	198–201	205–208[46]
4	**5d**	20	96	207–209	210–212[46]
5	**5e**	20	96	180–183	181–183[47]
6	**5f**	15	99	248–249	248–250[46]
7	**5g**	25	95	173–175	171–172[46]
8	**5h**	25	94	225–226	223–225[46]
9	**5i**	30	96	250–252	252–253[47]
10	**5j**	25	94	145–147	146–148[46]
11	**5k**	20	92	240–242	242–243[47]
12	**5l**	25	95	220–222	223–224[46]
13	**5m**	20	94	191–192	190–193[46]
14	**5n**	30	90	180–182	175–178[46]
15	**5o**	30	93	171–173	171–173[46]

[a]Aromatic aldehydes **1** (1.0 mmol), hydrazine hydrate **2** (0.03 g, 1.0 mmol), ethyl acetoacetate **3** (0.14 g, 1.0 mmol), malononitrile **4** (0.07 g, 1.0 mmol) and NFS-PRS (0.03 g) at room temperature in water.

(containing the product).[48] The separated catalyst was washed with acetone and dried at 100°C under vacuum for 2 h and reused five times for the same reaction to afford 98%, 98%, 97%, 95% and 94% yields, respectively.

In summary, NFS-PRS has been used as an efficient, re-usable and green solid acid catalyst for the one-pot synthesis of pyranopyrazole derivatives. Excellent yields, short reaction times, simplicity of operation and easy separation and re-usability of catalyst are some advantages of this method.

Experimental Section

All materials and reagents were purchased from Merck and Aldrich and used without further purification. Mps were determined on an Electrothermal type 9100 melting point apparatus and are uncorrected. The IR spectra were recorded on a Thermo Nicolet AVATAR-370 FT-IR spectrophotometer and ^{1}H NMR spectra were obtained on a Bruker DRX400 spectrometer.

Catalyst Preparation

Preparation of $NiFe_2O_4$ Nanoparticles

A solution of the two aqueous metallic salts (1 M of $FeCl_3$, 160 mL and 1 M of $NiCl_2$, 40 mL) was poured as quickly as possible into one liter of a boiling aqueous solution of 1M NaOH under vigorous stirring (700 rpm) using a mechanical stirrer. Then, the solution was cooled to room temperature and stirred continuously for 90 min. The resulting

precipitate was then purified by four repeated centrifugation (4000–6000 rpm, 20 min) with water (500 mL) and decantation.

Preparation of $NiFe_2O_4$@SiO_2 Core-shell

The $NiFe_2O_4$ NP (2.0 g, 8.57nbsp;mmol) was ultrasonically dispersed (Crest Ultrasonic Bath Model CP2600T) in ethanol (25 mL) for 2 h at 60°C and then a 25% aqueous ammonia (10 mL) was added to the mixture and stirred at 60°C for 40 min. Then tetraethyl orthosilicate (TEOS) (1.0 mL) was added (as the silica source) to the mixture and stirring was continued at the same temperature for 24 h. The suspended silica-coated MNP was separated from the solution by placing an external magnet on the outside of the flask and the remaining solution was decanted. The MNP was washed three times with methanol and dried in vacuum for 48 h. The resulting MNP ($NiFe_2O_4$@SiO_2) were then calcinated at 800°C for 4 h.

Preparation of Preyssler HPA ($H_{14}[NaP_5W_{30}O_{120}]$)

The Preyssler HPA ($H_{14}[NaP_5W_{30}O_{120}]$) was prepared as follows: A solution of 33 g (0.1 mole) $Na_2WO_4.2H_2O$ in 45 mL of water was stirred (200 rpm) at 45°C for 30 min. Then it was cooled to room temperature followed by the addition of 25 mL of 85% phosphoric acid and the resulting yellow solution was heated at reflux for 5 h. The solution was allowed to cool to room temperature, diluted with 50 mL of water and 10 g of potassium chloride was added with stirring (stir bar, 200 rpm). The mixture was stirred for 30 min at room temperature and then evaporated (rotary evaporator) to dryness (90°C). The solid obtained was dissolved in 75 mL of warm water (90°C) and upon cooling to room temperature, white crystals (15.4 g) of the potassium salt of Preyssler ($K_{14}[NaP_5W_{30}O_{120}]$) were formed. The free acid of Preyssler HPA ($H_{14}[NaP_5W_{30}O_{120}]$) was obtained by passage of a solution of 11.4 g of the potassium salt of Preyssler (obtained above) in 20 mL of water through a column (50 cm × 1 cm) of acidic Dowex 50W × 8 followed by evaporation of the eluate to dryness in vacuum overnight.[49–51]

Preparation of $NiFe_2O_4$@SiO_2-Preyssler (NFS-PRS)

The Preyssler HPA was immobilized on the $NiFe_2O_4$@SiO_2as follows. To a suspension of $NiFe_2O_4$@SiO_2 (1.0 g) in water (50 mL) was added dropwise a solution of Preyssler HPA (0.75 g) in water (5 mL) and the mixture was stirred (stir bar, 200 rpm) for 12 h at room temperature under N_2 atmosphere.Then the solvent was evaporated and the supported catalyst was collected and dried in vacuum overnight and the supported nano-catalyst (NFS-PRS) was calcinated at 250°C for 2 h.[43]

General Procedure for the Synthesis of Pyranopyrazole Derivatives (5a–o)

A mixture of the aromatic aldehyde (1.0 mmol), ethyl acetoacetate (0.14 g, 1.0 mmol), malononitrile (0.07 g, 1.0 mmol), hydrazine hydrate (100%, 0.03 g, 1.0 mmol) and NFS-PRS (0.03 g) in water (10 ml) was stirred (stir bar, 100 rpm) at room temperature for 15–30 min. Upon completion of the reaction, the nano-magnetic catalyst was separated from the reaction mixture using an external magnet (placed on the outside wall of the reaction vessel), washed with acetone (50 ml) and dried at 100°C for 2 h. It was re-used at least

five times without loss of activity. The solvent was evaporated from the decanted solution obtained from the isolation of the catalyst to give the pure products **5a–o** (see *Table 3*).

Procedure for Larger Scale Preparation of 5a

A mixture of the benzaldehyde (2.1 g, 20 mmol), ethyl acetoacetate (2.8 g, 20 mmol), malononitrile (1.4 g, 20 mmol), hydrazine hydrate (100%, 0.6 g, 20 mmol) and NFS-PRS (0.6 g) in water (200 ml) was stirred at room temperature for 15–30 min. Upon completion of the reaction, the nano-magnetic catalyst was separated from the reaction mixture using an external magnet as described above, washed with acetone (50 ml) and dried at 100°C for 2 h and re-used. The decanted solution obtained from the isolation of the catalyst was evaporated to give the pure product (**5a**) in 98% yield.

Analytical Data for Selected Compounds

6-Amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3c]pyrazole-5-carbonitrile (5a): IR: 3450, 3370, 2195, 1645, 1610, 1605, 1446; ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.91 (s, 3H), 4.74 (s, 1H), 6.98 (s, 2H), 7.45–7.16 (m, 5H), 11.98 (s, 1H); ^{13}C NMR (500 MHz, DMSO-d_6): δ 11.5, 25.1, 70.8, 112.0, 126.2, 127.4, 130.1, 131, 140.2, 144.1 152.3, 160.5.

6-Amino-3-methyl-4-(4-chlorophenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5b): IR: 3380, 3281, 2193, 1622, 1454; ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.80 (s, 3H), 4.59 (s, 1H), 6.7 (s, 2H), 7.20 (d, 2H), 7.31 (d, 2H), 12.1 (s, 1H); ^{13}C NMR (500 MHz, DMSO-d_6): δ 11.5, 24.3, 70.2, 112, 126.8, 127.3, 130.2, 134.4, 141.3, 142, 153.5, 160.6.

6-Amino-3-methyl-4-(4-methoxyphenyl)-1,4-dihydropyrano[2,3c]pyrazole-5-carbonitrile (5d): IR: 3480, 3259, 2181, 1610, 1442; ^{1}H NMR (500, $CDCl_3$): δ 1.78 (s, 3H), 3.85 (s, 3H), 4.60 (s, 1H), 6.88 (d, 2H), 6.89 (d, 2H), 7.20 (s, 2H), 12.08 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 10.1, 36.3, 55, 57.6, 107.7, 113.5, 114.3, 119, 136.8, 144.4, 156, 156.2, 160.5.

6-Amino-3-methyl-4-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5f): IR: 3439, 3378, 2180, 1651, 1597, 1516, 1456; ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.98 (s, 3H), 4.71 (s, 1H), 6.94 (s, 2H), 7.49 (d, 2H), 8.14 (d, 2H), 11.65 (s, 1H); ^{13}C NMR (500 MHz, DMSO-d_6): δ 11.4, 23.5, 70.8, 112.8, 128, 129, 130.1, 135.5, 141.8, 150.2, 154.2, 160.8.

6-Amino-3-methyl-4-(3-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5m): IR: 3388, 3280, 2185, 1622, 1455; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.82 (s, 3H), 4.99 (s, 1H), 6.97 (s, 2H), 7.85 (s, 1H), 7.78 (d, 1H), 7.42–7.45 (m, 2H), 12.16 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 9.8, 32.6, 59.8, 120.5, 121.6, 124.9, 128, 130.2, 134.3, 135.5, 142, 146.2, 148.8, 175.8.

Acknowledgments

The authors are grateful to Ferdowsi University of Mashhad for financial support.

References

1. N. Mizuno and M. Misono, *Chem. Rev.*, **98**, 199 (1998).
2. C. W. Lim and I. S. Lee, *Nano Today*, **5**, 412 (2010).

3. V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J. M. Basset, *Chem. Rev.*, **111**, 3036 (2011).
4. M. M. Lin, H. H. Kim, H. Kim, M. Muhammed and D. K. Kim, *Nano Rev.*, **1**, 4883 (2010).
5. D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.*, **44**, 7852 (2005).
6. A. Hu, G. T. Yee and W. Lin, *J. Am. Chem. Soc.*, **127**, 12486 (2005).
7. M. Mojtahedi, M. S. Abaee and T. Alishiri, *Tetrahedron Lett.*, **50**, 2322 (2009).
8. R. Hekmatshoar, M. M. Heravi, S. Sadjadi, H. A. Oskooie and F. F. Bamoharram, *Catal. Comm.*, **9**, 837 (2008).
9. A. Hafizi, A. Ahmadpour, M. M. Heravi and F. F. Bamoharram, *Nanotechnol. Eng. Med.*, **2**, 1004 (2012).
10. Y. B. Gu, R. P. Wei, X. Q. Ren and J. Wang, *Catal. Lett.*, **113**, 41 (2007).
11. S. Verma and S. L. Jain, *Terahedro. Lett.*, **53**, 6055 (2012).
12. S. Verma, S. L. Jain and B. Sain, *Beilstein J. Org. Chem.*, **7**, 1334 (2011).
13. S. Verma and S. L. Jain, *Tetrahedron Lett.*, **53**, 2595 (2012).
14. N. Kumar, S. Verma and S. L. Jain, *Chemistry Lett.*, **4**, 920 (2012).
15. S. Verma, S. L. Jain and B. Sain, *Org. Biomol. Chem.*, **9**, 2314 (2011).
16. S. Verma, S. L. Jain and B. Sain, *Tet. Lett.*, **51**, 6897 (2010).
17. S. Verma, S. Kumar, S. L. Jain and B. Sain, *Org. Biomol. Chem.*, **9**, 6943 (2011).
18. M. A. A. El Remaily and S. K. Mohamed, *Tetrahedron*, **70**, 270 (2014).
19. B. Myrboh, H. Mecadon, Md. R. Rohman, M. Rajbangshi, I. Kharkongor, B. M. Laloo, I. Kharbangar and B. Kshiar, *Org. Prep. Proced. Int.*, **45**, 253 (2013).
20. A. Domling, *Curr. Opin. Chem. Biol.*, **6**, 306 (2002).
21. N. Foloppe, L. M. Fisher, R. Howes, A. Potter, A. G. Robertson and A. E. Surgenor, *Bioorg. Med. Chem.*, **14**, 4792 (2006).
22. S. C. Kuo, L. J. Huang and H. Nakamura, *J. Med. Chem.*, **27**, 539 (1984).
23. J. L. Wang, D. Liu, Z. J. Zheng, S. Shan, X. Han, S. M. Srinivasula, C. M. Croce, E. S. Alnemri and Z. Huang, *Proc. Natl. Acad. Sci. U.S.A.*, **97**, 7124 (2000).
24. F. M. Abdelrazek, P. Metz, O. Kataeva, A. Jaeger and S. F. El−Mahrouky, *Arch. Pharm.*, **340**, 543 (2007).
25. S. A. El-Assiery, G. Hosni Sayed and A. Fouda, *Acta Pharm.*, **54**, 143 (2004).
26. M. A. A. El Remaily, *Tetrahedron*, **70**, 2971 (2014).
27. K. Kanagaraj and K. Pitchumani, *Tetrahedron. Lett.*, **51**, 3312 (2010).
28. H. Mecadon, M. R. Rohman, I. Kharbangar, B. M. Laloo, I. Kharkongor, M. Rajbangshi and B. Myrboh, *Tetrahedron Lett.*, **52**, 3228 (2011).
29. J. Ebrahimi, A. Mohammadi, V. Pakjoo, E. Bahramzade and A. Habibi, *J. Chem. Sci.*, **124**, 1013 (2012).
30. G. Santhosh Kumar, C. Kurumurthy, B. Veeraswamy, P. Sambasiva Rao, P. Shanthan Rao and B. Narsaiah, *Org. Prep. Proced. Int.*, **45**, 429 (2013).

31. H. R. Shaterian and M. Kangani, *Res. Chem. Inter.*, **40**, 1997 (2014).

32. K. Ablajan, L. Wang, Z. Maimaiti and Y. T. Lu, *Monatsh. Chem.*, **145**, 491 (2014).

33. B. Maleki and S. Sedigh Ashrafi, *RSC. Adv.*, **4**, 42873 (2014).

34. H. Eshghi, A. Khojastehnezhad, F. Moeinpour, Sh. Rezaeiana, M. Bakavoli, M. Teymouri, A. Rostami and K. Haghbeen, *Tetrahedron.*, **71**, 436 (2015).

35. B. Maleki, H. Eshghi, S. Sedigh Ashrafi, A. Khojastehnezhad, G. Esmailian Kahoo, R. Tayebee and F. Moeinpour, *RSC Adv.*, **5**, 64850 (2015).

36. H. Eshghi, A. Khojastehnezhad, F. Moeinpour, M. Bakavoli, S. M. Seyedi and M. Abbasi, *RSC Adv.*, **4**, 39782 (2014).

37. A. Khojastehnezhad, M. Rahimizadeh, F. Moeinpour, H. Eshghi and M. Bakavoli, *C. R. Chim.*, **17**, 459 (2014).

38. A. Khojastehnezhad, M. Rahimizadeh, F. Moeinpour, H. Eshghi and M. Bakavoli, *Chin. J. Cat.*, **35**, 376 (2014).

39. M. Ghiaci, M. Zarghani, A. Khojastehnezhad and F. Moeinpour, *RSC Adv.*, **4**, 15496 (2014).

40. B. Maleki, E. Sheikh, E. Rezaee Seresht, H. Eshghi, S. Sedigh Ashrafi, A. Khojastehnezhad and H. Veisi, *Org. Prep. Proced. Int.*, Accepted for publication (2016).

41. A. Khojastehnezhad, A. Davoodnia, M. Bakavoli, N. Tavakoli-Hoseini and M. Zeinali-Dastmalbaf, *Chin. J. Chem.*, **29**, 297 (2011).

42. M. Zeinali-Dastmalbaf, A. Davoodnia, M. M. Heravi, N. Tavakoli-Hoseini, A. Khojastehnezhad and H. A. Zamani, *Bull. Korean Chem. Soc.*, **32**, 656 (2011).

43. H. Eshghi, A. Javid, A. Khojastehnezhad, F. Moeinpour, F. F. Bamoharram, M. Bakavoli and M. Mirzaei, *Chin. J. Cat.*, **36**, 299 (2015).

44. I. V. Kozhevnikov, *Chem. Rev.*, **98**, 171 (1998).

45. J. F. Keggin, *Nature*, **131**, 908 (1933).

46. F. Tamaddon and M. Alizadeh, *Tetrahedron. Lett.*, **55**, 3588 (2014).

47. J. M. Khurana, B. Nand and S. Kumar, *Synth. Commun.*, **41**, 405 (2011).

48. D. Wang and D. Astruc, *Chem. Rev.*, **114**, 6949 (2014).

49. M. H. Alizadeh, S. P. Harmalker, Y. Jeannin, J. Martin and M. T. Pope, *J. Am. Chem. Soc.*, **107**, 2662 (1985).

50. F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib and M. Jahangir, *J. Mol. Catal.*, **252**, 90 (2006).

51. F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir and A. Gharib, *Appl. Catal.*, **302**, 42 (2006).