This article was downloaded by: [FU Berlin] On: 12 May 2015, At: 06:36 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



### Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

# An Environmentally Benign One-Pot Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones and -thiones Using Tetrabutylammonium Hexatungstate [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] as a Recyclable Catalyst

Neda Mohammadzadeh-Dehsorkh<sup>a</sup>, Abolghasem Davoodnia<sup>a</sup>, Niloofar Tavakoli-Hoseini<sup>a</sup> & Maryam Moghaddas<sup>a</sup>

<sup>a</sup> Department of Chemistry, Mashhad Branch , Islamic Azad University , Mashhad, Iran Published online: 07 Nov 2011.

To cite this article: Neda Mohammadzadeh-Dehsorkh , Abolghasem Davoodnia , Niloofar Tavakoli-Hoseini & Maryam Moghaddas (2011) An Environmentally Benign One-Pot Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones and -thiones Using Tetrabutylammonium Hexatungstate [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] as a Recyclable Catalyst, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:9, 1135-1140, DOI: <u>10.1080/15533174.2011.591358</u>

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2011.591358</u>

#### PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>



## An Environmentally Benign One-Pot Synthesis of 3,4-Dihydropyrimidin-2(1*H*)-ones and -thiones Using Tetrabutylammonium Hexatungstate [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] as a Recyclable Catalyst

Neda Mohammadzadeh-Dehsorkh, Abolghasem Davoodnia, Niloofar Tavakoli-Hoseini, and Maryam Moghaddas

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

Tetrabutylammonium hexatungstate  $[TBA]_2[W_6O_{19}]$ , an isopolytungstate, was found to be a highly efficient and recyclable heterogeneous catalyst for Biginelli reaction of ethyl acetoacetate, an aryl aldehyde, and urea or thiourea under solvent-free conditions, giving rise to 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones. Good to high yields, short reaction times, easy workup, and absence of any volatile and hazardous organic solvents are just a few of the advantages of this procedure. Furthermore, the catalyst can be recycled after a simple workup, and can be used at least three times without substantial reduction in its catalytic activity.

**Keywords** Biginelli reaction, heterogeneous catalysis, multicomponent reactions, solvent-free conditions, tetrabutylammonium hexatungstate [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>]

#### INTRODUCTION

Multicomponent reactions (MCRs) have attracted the attention of synthetic organic chemists for building highly functionalized organic molecules and pharmacologically important heterocyclic compounds in a very fast and efficient manner without the isolation of any intermediate.<sup>[1]</sup> Multicomponent condensations involve three or more compounds reacting in a single event, but consecutively to form a new product, which contains the essential parts of all the starting materials. Therefore, MCRs contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption, and waste production. Bigenilli,<sup>[2]</sup> Ugi,<sup>[3]</sup> Passerini,<sup>[4]</sup> and Mannich<sup>[5]</sup> reactions are some examples of MCRs.

Dihydropyrimidinones and -thiones have attracted considerable attention because of their wide spectrum of biological and therapeutic activities such as antiviral, antitumor, antibacterial, anti-inflammatory, anticancer, and antioxidant properties.<sup>[6-8]</sup> Additionally, their particular structure has been found in natural marine alkaloid batzalladines, which are the first low-molecularweight natural products reported in the literature to inhibit the binding of HIV gp-120 to the CD4 cell, thus disclosing a new path toward the development of AIDS therapy.<sup>[9]</sup> The first procedure for the synthesis of dihydropyrimidinones, reported by Biginelli in 1893, involves acid-catalyzed one-pot, threecomponent condensation of  $\beta$ -dicarbonyl compounds with an aromatic aldehyde and urea derivatives.<sup>[10]</sup> A major drawback to Biginelli's original reactions, however, was poor to moderate yields.<sup>[11]</sup> There are several improved methods for the synthesis of dihydropyrimidinones and -thiones by condensation of  $\beta$ -dicarbonyl compounds with an aromatic aldehyde and urea or thiourea in the presence of Lewis or protic acid promoters such as concentrated H<sub>2</sub>SO<sub>4</sub>,<sup>[12]</sup> trichloroisocyanuric acid,<sup>[13]</sup> In Br<sub>3</sub>,<sup>[14]</sup> N-butyl-N,N-dimethyl- $\alpha$ -phenylethylammonium bromide,  $^{[15]}$  [bmim][FeCl<sub>4</sub>],  $^{[16]}$  Ln(OTf)<sub>3</sub>, with Ln = Yb, Sc, La,  $^{[17]}$ Amberlyst-70,<sup>[18]</sup> and ZrCl<sub>4</sub> or ZrOCl<sub>2</sub>.<sup>[19]</sup> Among the available methods applied for the preparation of dihydropyrimidinones and -thiones, sometimes harsh reaction conditions, long reaction times, low yields of the products, use of harmful organic solvents, expensive reagents, and strongly acidic conditions limit their uses for this purpose. In addition, some of the catalysts are not recoverable and reusable materials. Therefore, the development of simple, efficient, high-yielding, and environmentally friendly methods using new catalysts for the Biginelli reaction is still necessary.

Polyoxometalates (POMs), constituting a large class of metal oxide molecules, are known to have a variety of sizes, structures, electrochemical properties, and chemical reactivities.<sup>[20]</sup> POMs have been extensively studied because they have many practical applications, such as catalysis,<sup>[21,22]</sup> molecular materials,<sup>[23]</sup> and corrosion inhibition.<sup>[24]</sup> In recent decades, uses of some POMs as catalysts for fine organic synthetic processes

Received 26 March 2011; accepted 22 April 2011.

The authors are thankful to Islamic Azad University, Mashhad Branch, for financial support.

Address correspondence to Abolghasem Davoodnia, Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran. E-mail: adavoodnia@mshdiau.ac.ir

have been developed and are important for industries related to fine chemicals,<sup>[25]</sup> including flavors, pharmaceuticals, and food industries.<sup>[26]</sup> Furthermore, the Lindqvist-type metal–oxygen clusters,  $M_6O_{19}^{2-}$  (M = W, Mo), and their functionalized compounds have fascinating chemical properties and photophysical properties, and diverse practical applications.<sup>[27,28]</sup>

In continuation of our studies on the development of novel synthetic methodologies in various organic reactions,<sup>[29]</sup> we wish to report here a solvent-free synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones catalyzed by tetrabutylammonium hexatungstate  $[TBA]_2[W_6O_{19}]$ , an isopolytungstate, as a green and effective heterogeneous catalyst (Scheme 1).



SCH. 1. Biginelli reaction catalyzed by [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>].

#### **EXPERIMENTAL**

#### **Chemicals and Apparatus**

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The infrared (IR) spectra were obtained using a 4300 Shimadzu spectrophotometer as KBr disks. The <sup>1</sup>H-nuclear magnetic resonance (NMR; 500 MHz) spectra were recorded with a Bruker DRX500 spectrometer.

TABLE 1 Effect of [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] amount on the model reaction in solvent-free conditions<sup>a</sup>

Entry	Catalyst (mol%)	Time (min)	Yield (%) <sup>b</sup>
	Cuturyst (mor/c)	Time (mm)	
1	None	120	None
2	0.7	25	40
3	0.9	25	68
4	1.3	25	93
5	2.0	25	80
6	2.6	25	60

<sup>a</sup>Ethyl acetoacetate (4 mmol), 4-chlorobenzaldehyde (4 mmol), and urea (5 mmol) at  $140^{\circ}$ C.

<sup>b</sup>Isolated yields.

TABLE 2 Synthesis of compound **4d** in the presence of  $[TBA]_2[W_6O_{19}]$ (0.1 g) at different temperatures in solvent-free conditions<sup>a</sup>

Entry	T (°C)	Time (h)	Yield (%) <sup>b</sup>
1	r.t	8	None
2	50	8	Trace
3	70	8	63
4	90	5	78
5	120	2	74
6	140	25 (min)	93

<sup>a</sup>Ethyl acetoacetate (4 mmol), 4-chlorobenzaldehyde (4 mmol), and urea (5 mmol).

<sup>b</sup>Isolated yields.

#### Synthesis Of Tetrabutylammonium Hexatungestate, [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>]

This catalyst was prepared according to the literature.<sup>[30]</sup> A mixture of sodium tungestate dihydate, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, (99%, 0.1 mol, 33 g), acetic anhydride (40 mL), and *N*,*N*-dimethylformamide (30 mL) is heated at 100°C for 3 h to obtain a white cream. Then a solution of acetic anhydride (20 mL) and HCl (12 *N*, 18 mL) in DMF (50 mL) is added with stirring, and the resulting mixture is filtered off to eliminate the undissolved white solid. A solution of tetrabutylammonium bromide (0.047 mol, 15.1 g) in methanol (50 mL) is added with rapid stirring to give a white precipitate. This suspension is stirred for 5 min and the product is filtered. Recrystallization from a minimum amount of hot dimethyl sulfoxide (DMSO) gives colorless diamond-shaped crystals.

#### General Procedure for the Synthesis of 3,4-Dihydropyrimidin-2(1*H*)-ones and -thiones 4a–n Using [TBA]<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>] as Catalyst

A mixture of ethyl acetoacetate 1 (4 mmol), an aryl aldehyde 2 (4 mmol), urea or thiourea 3 (5 mmol), and  $[TBA]_2[W_6O_{19}]$  (0.1 g, 0.053 mmol) was heated on the oil bath at 140°C for

 TABLE 3

 Effect of solvent on the model reaction<sup>a</sup>

Entry	Solvent	T (°C)	Time (h)	Yield (%) <sup>b</sup>
1	EtOH	Reflux	8	10
2	$H_2O$	Reflux	8	None
3	$CH_2Cl_2$	Reflux	8	12
4	CH <sub>3</sub> CN	Reflux	8	60
5	Cyclohexane	Reflux	8	None
6	Solvent-free	140	25 (min)	93

<sup>a</sup>Ethyl acetoacetate (4 mmol), 4-chlorobenzaldehyde (4 mmol), urea (5 mmol), and  $[TBA]_2[W_6O_{19}]$  (0.1 g).

<sup>b</sup>Isolated yields.

					Melting point (°C)			
Entry	Ar	Х	Product <sup>b</sup>	Time (min)	Yield (%) <sup>c</sup>	Found	Reported	Reference
1	3-BrC <sub>6</sub> H <sub>4</sub>	0	Eto NH Me NH H	30	87	192–193	195–196	[16]
2	4-BrC <sub>6</sub> H <sub>4</sub>	0		30	88	186–188	197	[15]
3	2-ClC <sub>6</sub> H <sub>4</sub>	0	4b	40	85	218–220	222–224	[14]
4	4-ClC <sub>6</sub> H <sub>4</sub>	0		25	93	216–217	212–214	[14]
5	4-FC <sub>6</sub> H <sub>4</sub>	0		36	86	178–180	173–176	[19a]
6	3-HOC <sub>6</sub> H <sub>4</sub>	Ο		38	80	175–177	163–165	[14]
7	4-HOC <sub>6</sub> H <sub>4</sub>	0	4f OH EtO Me NH H Ag	35	86	236–238	230–232	[14]

TABLE 4Synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones 4a-n catalyzed by  $[TBA]_2[W_6O_{19}]^a$ 

(Continued on next page)

#### N. MOHAMMADZADEH-DEHSORKH ET AL.

Ar	Х	Product <sup>b</sup>	Time (min)
4-MeOC <sub>6</sub> H <sub>4</sub>	0		25
	Ar 4-MeOC <sub>6</sub> H <sub>4</sub>	Ar X 4-MeOC <sub>6</sub> H <sub>4</sub> O	ArXProductb4-MeOC_6H_4O $\bigcap_{eto} H_{eto}$ $\bigoplus_{eto} H_{eto}$ $\bigoplus_{eto} H_{eto}$

TABLE 4	
Synthesis of 3,4-dihydropyrimidin-2(1 <i>H</i> )-ones and -thiones <b>4a–n</b> catalyzed by $[TBA]_2[W_6O_{19}]^a$ (Cont	inued)

Melting point (°C)

Entry	Ar	Х	Product <sup>b</sup>	Time (min)	Yield (%) <sup>c</sup>	Found	Reported	Reference
8	4-MeOC <sub>6</sub> H <sub>4</sub>	0		25	90	200–203	198–200	[19a]
9	4-MeC <sub>6</sub> H <sub>4</sub>	0	4h	25	92	209–212	214–216	[13]
10	2-CIC <sub>6</sub> H <sub>4</sub>	S	4i	35	80	166–168	168–169	[19b]
11	4-ClC <sub>6</sub> H <sub>4</sub>	S		35	83	190–193	192–194	[14]
12	4-FC <sub>6</sub> H <sub>4</sub>	S		38	81	190–191	191–192	[18]
13	4-MeOC <sub>6</sub> H <sub>4</sub>	S		30	90	151–152	150–152	[14]
14	4-MeC <sub>6</sub> H <sub>4</sub>	S	4m Me H Me NH Me NH Me S	37	80	180–183	189–192	[13]

<sup>a</sup>Ethyl acetoacetate (4 mmol), aryl aldehyde (4 mmol), urea or thiourea (5 mmol), and  $[TBA]_2[W_6O_{19}]$  (0.1 g) at 140°C.

<sup>&</sup>lt;sup>b</sup>All the products were characterized by IR spectral data and comparison of their melting points with those of authentic samples. Also, the structures of some products were confirmed by <sup>1</sup>H-NMR spectral data.

<sup>&</sup>lt;sup>c</sup>Isolated yields.

an appropriate time. The progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be recycled by a simple filtration. The product was collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **4a–n** in good to high yields.

#### **Recycling and Reusing of the Catalyst**

Due to the fact that the catalyst was insoluble in hot ethanol, it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold ethanol, dried at 60°C under vacuum for 1 h, and was reused in another reaction. The catalyst could be used at least three times with only slight reduction in its catalytic activity.

#### Selected <sup>1</sup>H-NMR and IR Data

Compound **4a** (Ar = 3-BrC<sub>6</sub>H<sub>4</sub>, X = O): <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.10 (t, 3H, J = 7.0 Hz, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 3.95–4.05 (m, 2H, CH<sub>2</sub>), 5.14 (d, 1H, J = 3.2 Hz, CH), 7.23 (d, 1H, J = 7.7 Hz, arom-H), 7.31 (t, 1H, J = 7.8 Hz, arom-H), 7.39 (s, 1H, arom-H), 7.45 (dt, 1H, J = 7.9, 0.9 Hz, arom-H), 7.77 (s, 1H, NH), 9.25 (s, 1H, NH). IR (KBr disk): v 3238 (NH), 3114 (NH), 1706 (C = O), 1654 (C = O) cm<sup>-1</sup>.

Compound **4d** (Ar = 4-ClC<sub>6</sub>H<sub>4</sub>, X = O): <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ ppm): 1.09 (t, 3H, *J* = 7.1 Hz, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 3.95–4.05 (m, 2H, CH<sub>2</sub>), 5.15 (d, 1H, *J* = 3.2 Hz, CH), 7.25 (d, 2H, *J* = 7.7 Hz, arom-H), 7.39 (d, 2H, *J* = 7.7 Hz, arom-H), 7.75 (s, 1H, NH), 9.22 (s, 1H, NH). IR (KBr disk):  $\upsilon$  3233 (NH), 3114 (NH), 1703 (C = O), 1650 (C = O) cm<sup>-1</sup>.

Compound **4e** (Ar = 4-FC<sub>6</sub>H<sub>4</sub>, X = O): <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.09 (t, 3H, J = 7.2 Hz, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 3.95–4.00 (m, 2H, CH<sub>2</sub>), 5.14 (d, 1H, J = 3.2 Hz, CH), 7.10-7.30 (m, 4H, arom-H), 7.73 (s, 1H, NH), 9.20 (s, 1H, NH). IR (KBr disk): v 3238 (NH), 3079 (NH), 1703 (C = O), 1650 (C = O) cm<sup>-1</sup>.

Compound **4m** (Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>, X = S): <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ ppm): 1.11 (t, 3H, *J* = 7.1 Hz, CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.72 (s, 3H, CH<sub>3</sub>O), 4.00 (q, 2H, *J* = 7.1 Hz, CH<sub>2</sub>), 5.11 (d, 1H, *J* = 3.6 Hz, CH), 6.89 (d, 2H, *J* = 8.6 Hz, arom-H), 7.12 (d, 2H, *J* = 8.6 Hz, arom-H), 9.57 (s, 1H, NH), 10.26 (s, 1H, NH). IR (KBr disk)  $\upsilon$  3314 (NH), 3169 (NH), 1667 (C = O) cm<sup>-1</sup>.

#### **RESULTS AND DISCUSSION**

The catalyst  $[TBA]_2[W_6O_{19}]$  was prepared according to Fournier's method.<sup>[30]</sup> We first selected the synthesis of compound **4d** as a model reaction to optimize the reaction conditions. The reaction was carried out by heating a mixture of ethyl acetoacetate (4 mmol), 4-chlorobenzaldehyde (4 mmol), and urea (5 mmol) in the presence of various amounts of  $[TBA]_2[W_6O_{19}]$ .

The catalyst has a significant effect on the yield of the reaction (Table 1). It could be seen that no product was produced in the absence of  $[TBA]_2[W_6O_{19}]$  even after 2 h (entry 1), while good results were obtained in the presence of  $[TBA]_2[W_6O_{19}]$ . Increasing the amount of the catalyst to 0.1 g, the yield of the product could be increased to 93% within the same time. Greater amounts of the catalyst were found to have an inhibitory effect on the formation of the product (entries 5 and 6). Therefore, the optimal amount of the catalyst was 0.1 g (1.3 mol% based on ethyl acetoacetate) (entry 4).

The same model reaction in the presence of 0.1 g of the catalyst was carried out at different temperatures in solvent-free conditions to assess the effect of temperatures on the reaction yield. It was observed that yield is a function of temperature since the yield was increased as the reaction temperature was raised (Table 2). At  $140^{\circ}$ C, the product **4d** was obtained in high yield.

Also, the reaction was carried out in various solvents (Table 3). As shown in Table 3, in comparison to conventional methods the yield of the reaction under solvent-free conditions is higher and the reaction time is shorter.

In order to evaluate the generality of this model reaction we then prepared a range of 3,4-dihydropyrimidin-2(1H)-ones and -thiones under the optimized reaction conditions. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the expected products in good to high yields in short reaction times. The kind of aldehyde had no significant effect on the reaction. The results are shown in Table 4.

Reusability of the catalyst was also investigated. The catalyst was recovered according to the procedure mentioned in experimental section and reused for next reactions. The obtained results are summarized in Table 5. As shown in this table, the catalyst could be used at least three times with only slight reduction in the catalytic activity.

Although we did not investigate the reaction mechanism, based on Kantevari's suggestion,<sup>[31]</sup> the tetrabutyl ammonium ion [(n-Bu)<sub>4</sub>N<sup>+</sup>] probably induces polarization of carbonyl group in aldehydes. On the other hands, Reinheimer and co-workers<sup>[32]</sup> reported that terminal oxygen atoms or the bridging oxygen atom in the polyoxometalate anion  $W_6O_{19}^{2-}$  are slightly basic and therefore can promote the reactions.

TABLE 5

Comparison of efficiency of  $[TBA]_2[W_6O_{19}]$  in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones after three uses

				Yield (%) <sup>a</sup>	
Entry	Ar	Х	First	Second	Third
<b>4</b> a	$3-BrC_6H_4$	0	87	86	86
4d	$4-ClC_6H_4$	Ο	93	92	90
4m	4-MeOC <sub>6</sub> H <sub>4</sub>	S	90	89	88

<sup>a</sup>Isolated yields.

#### CONCLUSION

 $[TBA]_2[W_6O_{19}]$ , a solid organic salt of isopolytungstate, showed high catalytic activity in the synthesis of 3,4dihydropyrimidin-2(1*H*)-ones and -thiones. This procedure offers several advantages including mild reaction conditions, high yields, and ease of workup, which makes it a useful and attractive protocol for the synthesis of these compounds. Furthermore, the catalyst can be recycled after a simple workup, and used at least three times with only slight reduction in its catalytic activity. It has also all advantages devoted to solvent-free reactions, namely, environmentally friendly conditions.

#### REFERENCES

- (a) Kappe, C.O. Acc. Chem. Res. 2000, 33, 879. (b) Liu, F.; Evans, T.; Das, B.C. Tetrahedron Lett. 2008, 49, 1578. (c) Davoodnia, A.; Bakavoli, M.; Moloudi, R.; Khashi, M.; Tavakoli-Hoseini, N. Monatsh. Chem. 2010, 141, 867. (d) Davoodnia, A.; Heravi, M.M.; Safavi-Rad, Z.; Tavakoli-Hoseini, N. Synth. Commun. 2010, 40, 2588. (e) Davoodnia, A.; Heravi, M.M.; Rezaei-Daghigh, L.; Tavakoli-Hoseini, N. Chin. J. Chem. 2010, 28, 429.
- (a) Jain, S.L.; Joseph, J.K.; Singhal, S.; Sain, B. J. Mol. Catal. A Chem. 2007, 268, 134. (b) Zeinali-Dastmalbaf, M.; Davoodnia, A.; Heravi, M.M.; Tavakoli-Hoseini, N.; Khojastehnezhad, A.; Zamani, H.A. Bull. Korean Chem. Soc. 2011, 32, 656. (c) Kamal, A.; Krishnaji, T.; Azhar, M.A. Catal. Commun. 2007, 8, 1929.
- (a) Trifilenkov, A.S.; Ilyin, A.P.; Kysil, V.M.; Sandulenko, Y.B.; Ivachtchenko, A.V. *Tetrahedron Lett.* 2007, *48*, 2563. (b) Nenajdenko, V.G.; Reznichenko, A.L.; Balenkova, E.S. *Tetrahedron* 2007, *63*, 3031. (c) Xiang, Z.; Luo, T.; Lu, K.; Cui, J.; Shi, X.; Fathi, R.; Chen, J.; Yang, Z. *Org. Lett.* 2004, *6*, 3155.
- (a) Krishna, P.R.; Dayaker, G.; Narasimha Reddy, P.V. *Tetrahedron Lett.* 2006, 47, 5977. (b) Andrade, C.K.Z.; Takada, S.C.S.; Suarez, P.A.Z.; Alves, M.B. *Synlett.* 2006, 1539.
- (a) Davoodnia, A.; Tavakoli-Nishaburi, A.; Tavakoli-Hoseini, N. *Bull. Korean Chem. Soc.* 2011, *32*, 635. (b) Azizi, N.; Torkiyan, L.; Saidi, M.R. *Org. Lett.* 2006, *8*, 2079. (c) Wu, H.; Shen, Y.; Fan, L.; Wan, Y.; Zhang, P.; Chen, C.; Wang, W. *Tetrahedron* 2007, *63*, 2404.
- 6. Kappe, C.O.; Fabian, W.W. Tetrahedron, 1997, 53, 2803.
- Mayer, T.U.; Tapoor, T.M.; Haggarty, S.J.; King, R.W.; Schreiber, S.L.; Mitchison, T.J. Science 1999, 286, 971.
- 8. Kappe, C.O. Eur. J. Med. Chem. 2000, 35, 1043.
- (a) Patil, A.D.; Kumar, N.V.; Kokke, W.C.; Bean, M.F.; Freyer, A.J.; Debrossi, C.; Mai, S.; Truneh, A.; Faulkner, D.J.; Carte, B.; Breen, A.L.; Hertzberg, R.P.; Johnson, R.K.; Westley, J.W.; Potts, B.C.M. *J. Org. Chem.* **1995**, *60*, 1182. (b) Snider, B.B.; Chen, J.; Patil, A.D.; Freyer, A. *Tetrahedron Lett.* **1996**, *37*, 6977.

- 10. Biginelli, P. Gazz. Chim. Ital. 1893, 23, 360.
- Barluenga, J.; Thomas, M.; Ballesterus, A.; Lopez, A. Tetrahedron Lett. 1989, 30, 4573.
- Hassani, Z.; Islami, M.R.; Kalantari, M. Bioorg. Med. Chem. Lett. 2006, 16, 4479.
- Bigdeli, M.A.; Jafari, S.; Mahdavinia, G.H.; Hazarkhani, H. Catal. Commun. 2007, 8, 1641.
- Fu, N.Y.; Yuan, Y.F.; Cao, Z.; Wang, S.W.; Wang, J.T.; Peppe, C. *Tetrahe*dron 2002, 58, 4801.
- Reddy, K.R.; Reddy, C.V.; Mahesh, M.; Raju, P.V.K.; Reddy, V.V.N. *Tetra*hedron Lett. 2003, 44, 8173.
- 16. Chen, X.; Peng, Y. Catal. Lett. 2008, 122, 310.
- 17. Ma, Y.; Qian, C.T.; Wang, L.M.; Yang, M. J. Org. Chem. 2000, 65, 3864.
- 18. Chandak, H.S.; Lad, N.P.; Upare, P.P. Catal. Lett. 2009, 131, 469.
- (a) Reddy, C.V.; Mahesh, M.; Raju, P.V.K.; Babu, T.R.; Reddy, V.V.N. *Tetrahedron Lett.* **2002**, *43*, 2657. (b) Rodriguez-Dominguez, J.C.; Bernardi, D.; Kirsch, G. *Tetrahedron Lett.* **2007**, *48*, 5777.
- Pope, M.T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
- 21. Mizuno, N.; Misono, M. Chem. Rev. 1998, 98, 199.
- 22. Sadakane, M., Steckhan, E. Chem. Rev. 1998, 98, 219.
- 23. Coronado, E.; Gomez-Garcia, C.J. Chem. Rev. 1998, 98, 273.
- 24. Katsoulis, D.E. Chem. Rev. 1998, 98, 359.
- Kozhevnikov, I.V. In Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates 2, ed. E. Derouane; Wiley: New York, 2002.
- 26. Okuhara, T.; Mizuno, N.; Misono, M. Adv. Catal. 1996, 41, 113.
- (a) Pope, M.T. Heteropoly and Isopoly Oxometalates; Springer-Verlag: New York, 1983. (b) Pope, M.T. In Progress in Inorganic Chemistry, ed. S.J. Lippard; Wiley: New York, 1991, pp. 39, 181. (c) Hill, C.L. J. Mol. Catal. A Chem. 1996, 114, 1. (d) Hill, C.L. Chem. Rev. 1998, 98, 1.
- (a) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, *77*. (b) Strong, J.B.; Yap, G.P.A.; Ostrander, R.; Liable-Sands, L.M.; Rheingold, A.L.; Thouvenot, R.; Gouzerh, P.; Maatta E.A. J. Am. Chem. Chem. **2000**, *122*, 639.
- (a) Davoodnia, A.; Bakavoli, M.; Barakouhi, G.; Tavakoli-Hoseini, N. Chin. Chem. Lett. 2007, 18, 1483. (b) Davoodnia, A.; Roshani, M.; Malaeke, S.H.; Bakavoli, M. Chin. Chem. Lett. 2008, 19, 525. (c) Davoodnia, A.; Heravi, M.M.; Rezaei-Daghigh, L.; Tavakoli-Hoseini, N. Monatsh. Chem. 2009, 140, 1499. (d) Davoodnia, A.; Bakavoli, M.; Moloudi, R.; Khashi, M.; Tavakoli-Hoseini, N. Chin. Chem. Lett. 2010, 21, 1. (e) Davoodnia, A.; Allameh, S.; Fakhari, A.R.; Tavakoli-Hoseini, N. Chin. Chem. Lett. 2010, 21, 550. (f) Davoodnia, A. Asian J. Chem. 2010, 22, 1595.
- Fournier, M. In *Inorganic Synthesis*, ed. A.P. Ginsberg; John Wiley: New York, **1990**, pp. 27, 80.
- Chary, M.V.; Keerthysri, N.C.; Vupallapati, S.V.N.; Lingaiah, N.; Kantevari, S. Catal. Commun. 2008, 9, 2013.
- Reinheimer, E.W.; Fourmigue, M.; Dunbar, K.R. J. Chem. Crystallogr. 2009, 39, 723.