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Polyoxometalate Tri-supported Transition Metal Complexes를 이용한 Dihydropyrimidinones의 one-pot 합성

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One-pot Synthesis of Dihydropyrimidinones Using Polyoxometalate Tri-supported Transition Metal Complexes

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요 약. Vanadium 치환체인 polyoxometalate **1**, $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$을 가지고 있는 inorganic-organic complex의 촉매 활성도를 Biginelli 반응에 적용하여 연구하였다. Dihydropyrimidinones를 one-pot 합성하는 반응에서, $H_3PMo_{12}O_{40}$ 촉매 보다$[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$ 촉매가 더 좋은 결과를 나타내었다.

주제어: Keggin molybdenum-vanadium heteropolyoxoanions, Dihydropyrimidinones (DHPMs), Polyoxometalates (POMs), 유-무기 착물

ABSTRACT. The catalytic activity of an inorganic-organic complex with a vanadium-substituted polyoxometalate **1**, formulated as $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$ was studied in the Biginelli reactions. The obtained results showed that, in the one-pot synthesis of dihydropyrimidinones, the turnover frequencies (TOF) for the $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$ catalyst were higher than the $H_3PMo_{12}O_{40}$ catalyst.

Keywords: Keggin molybdenum-vanadium heteropolyoxoanions, Dihydropyrimidinones (DHPMs), Polyoxometalates (POMs), inorganic-organic complex

INTRODUCTION

Recently, much work has been focused on the rational construction of new organic-inorganic complexes based on polyoxometalates (POMs) and transition metal complexes due to their intriguing structures and potential applications in many areas.[1-7] In these complexes, POMs can coordinate to "secondary" transition metal atoms with organic moieties using their terminal or bridging oxygen atoms to stabilize frameworks. Meanwhile, transition metal complexes with diverse structural arrangements not only serve as charge-compensating units but also modify the wide-ranging properties of POMs, such as magnetic and optical properties, electronic conductivities and electrocatalysis.[1,8-13]

POM supported TMCs, $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$, is constructed from bi-capped Keggin molybdenum-vanadium heteropolyoxoanions and copper complex fragments.[14] The molybdenum-vanadium cluster $[PMo_8V_6O_{42}]^{6-}$ is based on the alpha-Keggin anion $[PMo_8V_4O_{40}]^{10-}$ capped with two $[VO]^{2+}$ ions. In the α-Keggin anion, there exit four trimetallic groups, each of which is composed of one VO_5 square pyramid and two MoO_6 octahedra via edge-sharing mode. The molybdenum-vanadium cluster $[PMo_8V_6O_{42}]^{6-}$ is based on the α-Keggin anion $[PMo_8V_4O_{40}]^{10-}$ capped with two $[VO]^{2+}$ ions. In the α-Keggin anion, there exit four trimetallic groups, each of which is composed of one VO_5 square pyramid and two MoO_6 octahedra via edge-sharing mode (*Fig*. 1). The bond valence sum calculations indicate that the polyoxoanion to be formulated as $[PMoMo_8^{IV}V_1^{V}V_3^{IV}O_{40}(V^{IV}O)_2]^{6-}$, in agreement with the XPS spectrum analysis.[14]

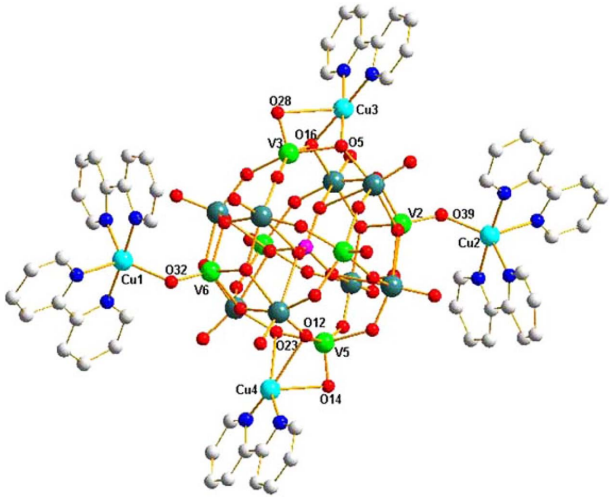


***Fig.* 1.** The bi-capped molybdenum-vanadium cluster tri-supported TMC in compound **1**. All water molecules and hydrogen atoms are omitted for clarity.

Dihydropyrimidin-2(1*H*)-ones (DHPMs), "Biginelli compounds", and their derivatives are known to exhibit therapeutic and pharmacological properties[15] including antiviral,[16] antitumor,[17] antibacterial,[18] anticancer,[19] antioxidant,[20] antihypertensive,[21] anti-inflammatory,[22,23] neuropeptide antagonists,[21] agents in treating anxiety[24] and optic nerve dysfunction.[25] Therefore, realizing the importance of 3,4-dihydropyrimidine-2-(1H)-ones in the synthesis of various drug sources many synthetic methods have been developed. These methods involve the use of catalysts like, $[Al(H_2O)_6](BF_4)_3$,[26] $Y(OAc)_2$. xH_2O,[27] $Cu(NO_3)_2$. $3H_2O$,[28] $CdCl_2$[29] and the use of microwave technique.[30]

The development of efficient and versatile catalytic systems for Biginelli reaction is an active ongoing research area and thus, there is scope for further improvement toward milder reaction conditions, variations of substituents in all three components and better yields.

In continuation of our previously reported catalytic properties of heteropoly acids, (HPAs),[31-33] herein, we wish to report a suitable method for the Biginelli three-component one-pot synthesis in our laboratory (*Scheme* 1).

RESULTS AND DISSCUSION

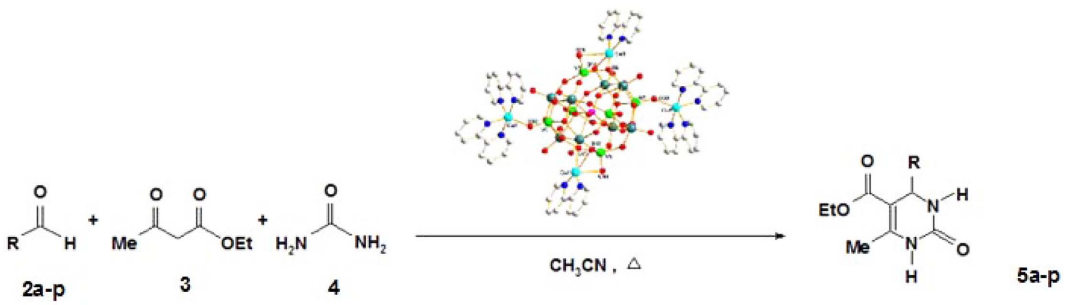
Characterization of $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$ (1)

FTIR: In the IR spectrum of **1** (*Fig*. 2), the bands at 1051 and 1034 cm^{-1} are ascribed to P-O stretching vibrations. The strong bands at 938 and 896 cm^{-1} are associated with $\nu(M\text{-}O_t)$ (M represents Mo or V), and those at 788 and 727 cm^{-1} are due to $\nu(M\text{-}O_a)$.[34] A series of bands in the range 1100-1600 cm^{-1} are characteristic of 2,2′-bipy.[14] Besides, there are additional bands at 668 and 610 cm^{-1} attributed to the asymmetry of Keggin anion affected by the covalent cation $[Cu(2,2'\text{-bipy})]^{2+}$ and $[Cu(2,2'\text{-bipy})2]^{2+}$.

XRD: X-ray powder analysis is widely used to study the structure of heteropoly complexes. The X-ray diffraction pattern of **1** is shown in *Fig*. 3.

Uv-vis: The UV-Vis spectrum of **1** is displayed in *Fig*. 4. The two bands near 230 and 295 nm are attributed to the ligand-to-metal charge transfers of $O_t \rightarrow M$ and $\mu_2\text{-}O \rightarrow M$ (M=V or W), respectively, where electrons are promoted from the low energy electronic states, mainly comprising of oxygen 2p orbitals, to the high-energy states, which mainly comprises of metal d orbitals.[35] The peak at 357 nm can be assigned to the d–d transition of WO_6 octahedra.[36,37]

TG: The thermal stability of **1** was investigated on crystalline samples under air atmosphere from 50-350 ºC (*Fig*. 5). The TGA curve indicates the weight loss of $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5\ H_2O$ can be divided into two steps. The first weight loss of 0.96% from 65 to 120 ºC, may be assigned to the removal of all non-coordinated water molecules (1.5 H_2O), which is in agreement with the calculated value 0.98 %. The second weight loss of 16.99% at 305-462 ºC may be ascribed to decomposition of three molecule of 2,2′-bipy, which is in agreement with the calculated value 17.07%. The overall weight



***Scheme* 1.**

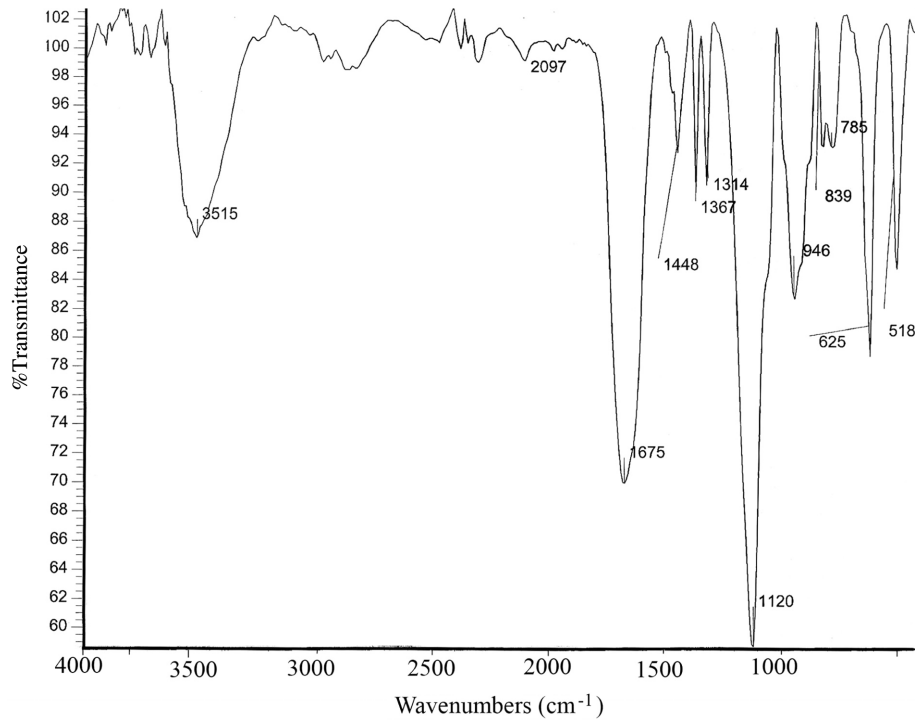


Fig. **2.** FTIR spectra of **1**.

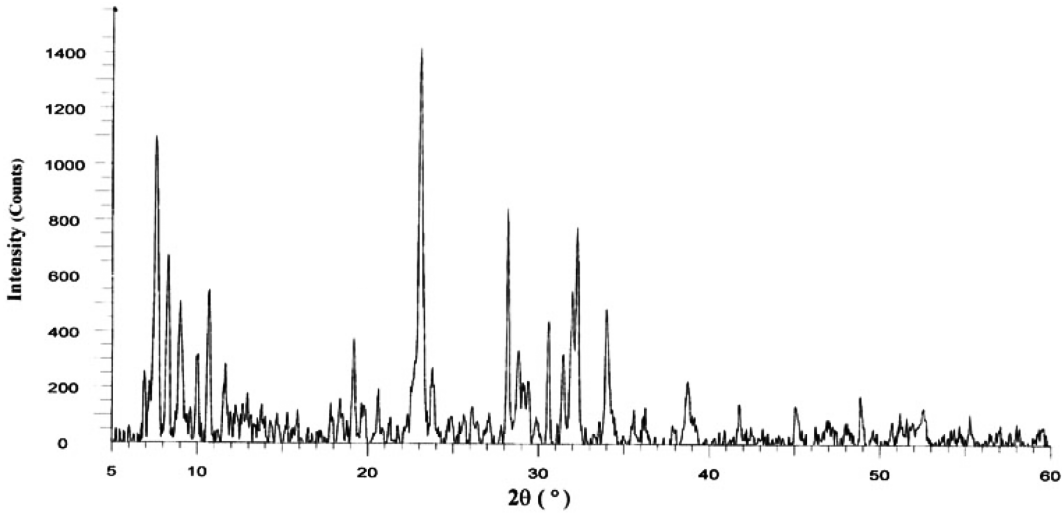


Fig. **3.** XRD patterns of **1**.

loss of 17.95% is accordant with the calculated value of 2,2′-bipy and water molecules of 18.5% in compound **1**.

Synthesis of dihydropyrimidinones in the presence of catalytic amounts of 1

In choosing the reaction media, different solvents were investigated in the synthesis of dihydropyrimidinones with $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$. Among the studied solvents, CH_3CN was chosen as suitable solvent because higher dihydropyrimidinone derivatives (*Table* 1). We also investigated the effect of reaction temperature on the synthesis of dihydropyrimidinones with **1**. It was observed that in the reaction of ethyl acetoacetone, 4-nitrobenzaldehyde and urea catalyzed by **1**, as a model reaction, only good yields of products were detected in the reaction mixture at room temperature. While, by increasing the reaction temperature (45 °C) the conversion increased.

Various aromatic aldehydes reacted to give the corresponding dihydropyrimidinones in moderate to excellent

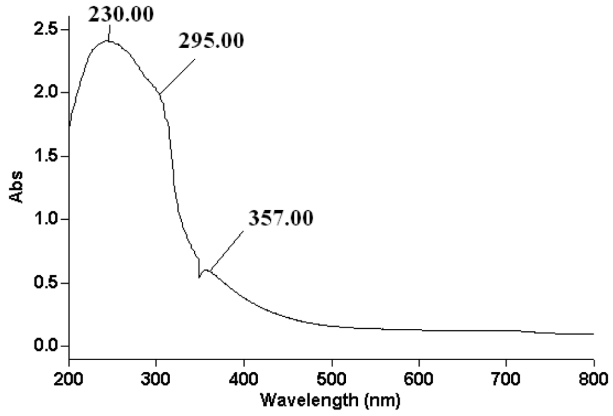


***Fig.* 4.** Uv-Vis spectra of **1.**

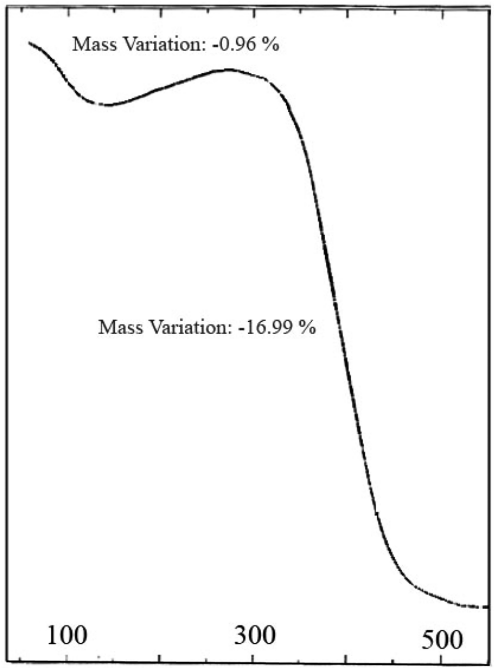


***Fig.* 5.** TG analysis of **1.**

yields (*Table* 2). Many pharmacologically relevant substitution patterns could be introduced on the aromatic ring with high efficiency. Most importantly, aromatic aldehydes carrying either electron donating (*Table* 2: 5i and 5j, 85-95%) or electron-withdrawing (*Table* 2: 5b-5h, 86-98%) substituents all reacted very well, giving moderate to excellent yields. Even for aliphatic aldehydes, which normally show extremely poor yields in the Biginelli reaction, better yields of the corresponding dihydropyrimidin-2(1H)-ones (*Table* 2: 5n, 5o, 88-90%) could be obtained.

In order to show the merit of the present work in comparison with recently reported protocols, we compared the results of the dihydropyrimidinones derivative synthesis from various aldehydes in the presence of $H_3PW_{12}O_{40}$, $[Al(H_2O)_6](BF_4)_3$. xH_2O, $Cu(NO_3)_2$. $3H_2O$ and $CdCl_2$ with respect to the amounts of the catalysts used, reaction times and yields of the products (*Table* 3). Comparison of compound **1** with these catalysts for this reaction show that activity of **1** seems to be higher than or equal with other known catalysts (*Table* 3).

In order to show the effect of hybridization on the catalytic activity of $H_3PMo_{12}O_{40}$ in the Biginelli reactions, all reactions were repeated with the same reaction conditions in the presence of $H_3PMo_{12}O_{40}$ as the catalyst. It was found that the hybrid catalyst gave higher conversions (TOFs) than unhybridized $H_3PMo_{12}O_{40}$ complex.

EXPERIMENTAL

Materials and measurements

All materials were commercial reagent grade. $H_3PW_{12}O_{40}$ (HPW) was purchased from Aldrich chemical company. FT-IR spectra were obtained as potassium bromide pellets in the range 400-4000 cm^{-1} with Nicolet *Impact 400 D*. ^1H NMR spectra were recorded with a Bruker-Avance AQS 300 MHZ. The melting points were determined using an electrothermal digital melting point apparatus and are uncorrected. Reaction courses and product mixtures were monitored by thin layer chromatography. The X-ray powdered diffraction patterns were taken on a Bruker-D8 advance with automatic control. The patterns were run with monochromatic Cu Kα (1.5406 Å) radiation with a scan rate of 2^o min^{-1}.

Preparation of $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$, 1

Compound **1** was hydrothermally synthesized in 60%

***Table* 1.** Synthesis of dihydropyrimidinones using $[Cu(2,2'\text{-bipy})][Cu(2,2'\text{-bipy})_2]_2[PMo_8V_6O_{42}]\cdot 1.5H_2O$; **1** in different solvents under reflux conditions.[a]

Temperature	Yield[b] (%) after 2h					
	H_2O	CH_2Cl_2	CH_3CH_2OH	CH_3OH	CH_3CN	Acetone
Room temperature	30	48	45	65	82	65
45 °C	65	70	65	75	98	72

[a]Reaction conditions: ethyl acetoacetone (1 mmol), 4-nitrobenzaldehyde (1 mmol), urea (1.5 mmol), catalyst, **1** (3mol %) and solvent (5 mL). [b]Isolated yield.

***Table* 2.** Synthesis of DHPMs using [Cu(2,2′-bipy)][Cu(2,2′-bipy)$_2$]$_2$[PMo$_8$V$_6$O$_{42}$]·1.5H$_2$O; **1** as catalysts.[a]

DHPMs	Substrate (R)	Time (h)	Yield (%)[b,c]	TOF	Mp (°C)	
					Reported [31]	Found
5a	4-Me-C$_6$H$_5$	1.0	98	4.90	211-216	213-215
5b	4-NO$_2$-C$_6$H$_5$	0.6	98	8.16	208-210	208-210
5c	3-NO$_2$-C$_6$H$_5$	1.2	95	3.96	217-219	218-220
5d	2-NO$_2$-C$_6$H$_5$	1.0	95	4.75	220-222	220-222
5e	4-Cl-C$_6$H$_5$	0.68	95	6.99	216-218	219-221
5f	2-Cl-C$_6$H$_5$	1.0	86	4.30	215-217	214-216
5g	4-OH-C$_6$H$_5$	1.6	90	2.81	227-229	227-229
5h	2-OH-C$_6$H$_5$	1.3	95	3.65	200-202	203-205
5i	4-MeO-C$_6$H$_5$	1.0	95	4.75	203-205	203-205
5j	3-MeO-C$_6$H$_5$	1.1	84	3.82	201-203	200-202
5k	Ph-CH=CH	1.8	91	2.53	229-231	224-226
5l	Ph-CH-CH$_2$	2.1	81	1.93	156-158	153-155
5m	3-Furfuryl	2.0	87	2.18	205-207	208-210
5n	n-Bu	4.7	90	1.01	154-156	154-156
5o	i-Pr	3.4	88	1.29	201-203	203-205
5p	Me	3.8	92	1.21	201-203	200-202

[a]Reaction conditions: [Cu(2,2′-bipy)][Cu(2,2′-bipy)$_2$]$_2$[PMo$_8$V$_6$O$_{42}$]·1.5H$_2$O (0.02 mmol), ethyl acetoacetate (1 mmol), aldehyde (1 mmol) and urea (1.5 mmol) were carried out in a one-pot condensation employing CH$_3$CN (5 mL) as the solvent at 45°C.
[b]Isolated yield.
[c]Identification of the products was ascertained by NMR and IR analysis.

***Table* 3.** Comparision of compound **1** with several catalysts for synthesis of dihydropyrimidinone derivatives with aromatic aldehydes, urea and ethyl acetoacetate.

Entry	Catalyst	Aromatic aldehydes (Ar-CHO) time (h) : Yield (%)		
		Ar=4-(NO$_2$)-C$_6$H$_4$	Ar=4-(Cl)-C$_6$H$_4$	Ar=2-(Cl)-C$_6$H$_4$
1	**1** [this work]	0.6 : 98	0.68 : 95	1 : 86
2	H$_3$PMo$_{12}$O$_{40}$ [31]	3.5 : 97	5 : 82	6 : 88
3	[Al(H$_2$O)$_6$](BF$_4$)$_3$ [26]	20 : 85	21 : 81	20 : 88
4	Y(OAc)$_2$·xH$_2$O [27]	4.5 : 92	4.5 : 91	3 : 98
5	Cu(NO$_3$)$_2$·3H$_2$O [28]	0.67 : 96	0.83 : 95	-
6	CdCl$_2$ [29]	5.3 : 89	5 : 89	5.6 : 85

yield (based on Mo). A mixture of Na$_2$MoO$_4$·2H$_2$O (0.73 g, 3.0 mmol), NH$_4$VO$_3$ (0.35 g, 3.0 mmol), CuSO$_4$·5H$_2$O (0.75 g, 3.0 mmol), 2,2′-bipy (0.117 g, 0.75 mmol), H$_2$C$_2$O·2H$_2$O (0.38 g, 3.0 mmol) and distilled water (13.5 mL, 750 mmol) in a molar ratio of 4:4:4:1:4:1000 was stirred for 120 min. The pH of the mixture was adjusted to 4 with dilute H$_3$PO$_4$ solution. The resultant mixture was sealed in a 20 mL Teflon-lined autoclave and heated at 170 °C for 96 h. The autoclave was then cooled to room temperature. The crystalline product was filtered, washed with distilled water and dried at ambient temperature to give 0.73 g solids.[14]

General procedure for the synthesis of dihydropyrimidinones, 5

In the presence of **1** (0.02 mmol), the reaction of ethyl acetoacetate **3** (1 mmol), aldehyde **2** (1 mmol) and urea **4** (1.5 mmol) were carried out in a one-pot condensation employing refluxing CH$_3$CN (5 mL) as the solvent (*Scheme* 1) for the appropriate time (*Table* 2). After the reaction was completed, as indicated by TLC analysis, the solvent was evaporated, the residue was dried and washed with water and the resulting solid was treated with hot EtOH and filtered again. The filtrate was concentrated to afford the recrystallized product. The products were characterized by IR and ^{1}HNMR spectral data and by comparison with melting points of the reported compounds.

Spectroscopic data of some 3,4-dihydropyrimidin-2(1H)-ones

Ethyl-6-methyl-4-(4-methylphenyl)-2-oxo-1,2,3,4-

tetrahydropyrimidine-5-carboxylate (5a): mp 213-215 °C; IR (KBr): ν [cm^{-1}] 3326, 3152, 1691, 1562, 1232, 1051, 783; ^{1}H NMR (DMSO-d_6) δ (ppm): 1.12 (t, J = 7.5 Hz, 3H), 2.28, 2.30 (s, 3H), 4.00 (q, J = 7.5 Hz, 2H), 5.11 (d, J = 3.0 Hz, 1H), 7.25 (m, 4H), 7.70 (br s, 1H, NH), 9.19 (br s, 1H, NH).

Ethyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5b): mp 208-210 °C; IR (KBr): ν [cm^{-1}] 3230, 3120, 1730, 1710, 1650; ^{1}H NMR (DMSO-d_6) d (ppm): 1.11 (t, J = 7.5 Hz, 3H), 2.29 (s, 3H), 4.00 (q, J = 7.5 Hz, 2H), 5.29 (d, J = 3.0 Hz, 1H), 7.51 (d, J = 10Hz, 2H), 7.91 (br s, 1H), 8.23 (d, J = 8.76 Hz, 2H, arom CH), 9.37 (s, 1H, NH).

Ethyl-6-methyl-4-(3-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5c): mp 2178-220 °C; IR (KBr): ν [cm^{-1}] 3300, 3120, 1710, 1690, 1630; ^{1}H NMR (DMSO-d_6) d (ppm): 1.11 (t, J = 7.5 Hz, 3H), 2.29(s, 3H), 4.02 (q, J = 7.5 Hz, 2H), 5.31 (d, J = 3.0 Hz, 1H), 7.65-7.75 (m, 2H), 7.95 (br s, 1H), 8.09-8.20 (m, 2H), 9.34 (br s, 1H).

Ethyl-6-methyl-4-(2-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5d): mp 220-222 °C; IR (KBr): ν [cm^{-1}] 3240, 3100, 1710, 1650; ^{1}H NMR (DMSO-d_6) d (ppm): 0.94 (t, J = 7.5 Hz, 3H), 2.30 (s, 1H), 3.88 (q, J = 7.5 Hz, 2H), 5.81 (d, J = 3.0 Hz, 1H), 7.49-7.98 (m, 5H), 9.39 (br s, 1H).

Ethyl-6-methyl-4-(4-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5e): mp 219-221 °C; IR (KBr): ν [cm^{-1}] 3220, 3100, 1720, 1700; ^{1}H NMR (DMSO-d_6) d (ppm): 1.10 (t, J = 7.2, 3H), 22 (s, 3H), 3.96 (q, J = 7.2, 2H), 5.02 (s, J = 3.2, 1H), 6.64 (d, J = 8.4, 2H), 7.02 (d, J = 8.4, 2H), 7.57 (s, 1H), 9.07 (s, 1H).

Ethyl-6-methyl-4-(2-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5f): mp 214-216 °C; IR (KBr): ν [cm^{-1}] 3360, 3220, 1690, 1640; ^{1}H NMR (DMSO-d_6) d (ppm): 1.08 (t, J = 7.5 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3) 3.91 (q, J = 7.5 Hz, 2H, OCH2), 5.67 (d, J = 2.5 Hz, 1H), 7.22-7.46 (m, 4H, arom H), 7.72 (br s, 1H, NH), 9.30 (br s, 1H, NH).

CONCLUSIONS

In conclusion, we have developed an economical and simple procedure for the synthesis of dihydropyrimidinones/thiones with high yields and short reaction times using [Cu(2,2′-bipy)][Cu(2,2′-bipy)$_2$]$_2$[$PMo_8V_6O_{42}$]·1.5H_2O as the catalyst in acetonitrile at 45 °C. Besides its simplicity, neutral reaction conditions and use of commercial solvents without previous purifications or drying, this method was effective with a variety of substituted aromatic aldehydes independently of the nature of the constituents in the aromatic ring, representing an improvement to the classical Biginelli's methodology.

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REFERENCES

1. Hagra-man, P. J.; Hagraman, D.; Zubieta, J. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2638.
2. Piepenbrink, M.; Triller, M. U.; Gorman, N. H. J.; Krebs, B. *Angew. Chem*. **2002**, *114*, 2633.
3. Stupp, S. I.; Braun, P. V. *Science* **1997**, *277*, 1242.
4. Khan, M. I.; Tabussum, S.; Doedens, R. J.; Golub, V. O.; O'Connor, C. J. *Inorg. Chem*. **2004**, *43*, 5850.
5. (a) Hegetschweiler, K.; Morgenstern, B. Zubieta, J.; Hagrman, P. J.; Lima, N.; Sessoli, R.; Totti, F. *Angew. Chem.* **2004**, *116*, 3518. (b) Hegetschweiler, K.; Morgenstern, B.; Zubieta, J.; Hagrman, P. J.; Lima, N.; Sessoli, R.; Totti, F. *Angew. Chem. Int. Ed*. **2004**, *43*, 3436.
6. Shivaiah, V.; Nagaraju, M.; Das, S. K. *Inorg. Chem*. **2003**, *42*, 6604.
7. Whitfield, T.; Wang, X.; Jacobson, A. J. *Inorg. Chem*. **2003**, *42*, 3728.
8. Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev*. **2000**, *100*, 853.
9. Swiegers, G. F.; Malefetse, T. J. *Chem. Rev*. **2000**, *100*, 3483.
10. Kitagawa, S.; Kitaura, R.; Noro, S. I. *Angew. Chem. Int. Ed*. **2004**, *43*, 2334.
11. Moulton, B.; Zaworotko, M. J. *Chem. Rev*. **2001**, *101*, 1629.
12. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
13. Li, C.; Cao, R.; O'Halloran, K. P.; Ma, H.; Wu, L. *Electrochim. Acta* **2008**, *54*, 484.
14. Cui, J.-W.; Cui, X.-B.; Xu, J.-N.; Yu, H.-H.; Xu, J.-Q.; Duan, W.-J.; Wang, T.-G. *J. Mol. Struct*. **2008**, *891*, 35.
15. Kappe, C. O. *Tetrahedron* **1993**, *49*, 6937.
16. McKinstry, W.; Reading, E. H. *J. Franclin Inst*. **1944**, *237*, 422.
17. Kumsars, K.; Velena, A.; Dubrus, G.; Uldrikis, J. Zidermane, A. *Biokhimiya* **1971**, *36*, 1201.
18. Matsuda, T.; Hirao, I. *Nippon Kagaku Zasshi*, **1965**, *86*, 1195.
19. Kato, T. *Japn. Kokai Tokkyo Koho JP* **1984**, *59*, 190974 *Chem. Abstr*. **1985**, *102*, 132067.

20. Stefani, H. A.; Oliveira, C. B.; Almeida, R. B.; Pereira, C. M. P.; Braga, R. C.; Cella, R.; Borges, V. C.; Savegnago, L.; Nogueira, C. W. *Eur. J. Med. Chem.* **2006**, *41*, 513.
21. Atwal, K. S.; Rovnyak, G. C.; Schwartz, J.; Moreland, S.; Hedberg, A.; Gougoutas, J. Z.; Malley, M. F.; Floyd, D. M. *J. Med. Chem*. **1990**, *33*, 1510.
22. Sadanadam, Y. S.; Shetty, M. M.; Diwan, P. V. *Eur. J. Med. Chem.* **1992**, *27*, 87.
23. Jauk, B.; Pernat, T.; Kappe, C. O. *Molecules* **2000**, *5*, 227.
24. Horovitz, Z. P.; (E. R. Squibb, and Sons) *Eur. Pat. Appl. EP* **1990**, *400*, 665 [*Chem. Abstr*. **1991**, *115*, 64793].
25. Crosson, C. E.; Potter, D. E.; Ondetti, M. A.; Floyd, D.; Aberg, G. (Houston Biotechnology, Inc.; E. R. Squibb, and Sons) PCT Int. Appl. WO, **1990**, *6*, 118 (*Chem. Abstr*., **1991**, *114*, 157224w.
26. Litvic, M.; Vecenaj, I.; Ladisic, Z. M.; Lovric, M.; Vinkovic, V.; Filipan-Litvic, M. *Tetrahedron* **2010**, *66*, 3463.
27. Aridoss, G.; Jeong, Y. T. *Bull. Korean. Chem. Soc.* **2010**, *31*, 863.
28. Wang, D.-C.; Guo, H.-M.; Qu, G.-R. *Synth. Commun*. **2010**, *40*, 1115.
29. Narsaiah, A. V.; Nagaiah, B. K. *Synthesis* **2004**, *8*, 1253.
30. El-Rahman, N. M. A.; Fawzy, N. M.; Zaki, M. E. A. *Int. J. Pharm. Tech. Res*. **2009**, *1*, 857.
31. Fazaeli, R.; Tangestaninejad, S.; Aliyan, H.; Moghadam, M. *Appl. Catal. A*. **2006**, *309*, 44.
32. Fazaeli, R.; Tangestaninejad, S.; Aliyan, H. *Appl. Catal. A*. **2007**, *318*, 218.
33. Fazaeli, R.; Aliyan, H. *Appl. Catal. A*. **2007**, *331*, 78.
34. Kozhevnikov, I. V. *Catalysis by polyoxometalates, Catalysis For Fine Chemical Synthesis*; U. K. 2002; Vol. 2.
35. Yamase, T. *Chem. Rev.* **1998**, *98*, 307.
36. Neizer, R.; Trojanowski, C.; Mattes, R. *J. Chem. Soc., Dalton Trans.* **1995**, 2521.
37. Shivaiah, V.; Das, S. K. *Inorg. Chem*. **2005**, *44*, 8846.