Journal of the Korean Chemical Society
2013, *Vol. 57, No. 5*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2013.57.5.599

Solvent-Free Synthesis of Some1-Acetyl Pyrazoles

Ganesamoorthy Thirunarayanan[†,*] and Krishnamoorthy Guna Sekar[‡]
[†]*Department of Chemistry, Annamalai University, Annamalainagar-608 002, India.*
[*]*E-mail: drgtnarayanan@gmail.com*
[‡]*Department of Chemistry, National College, Tiruchirappalli-620 001, India.*
(Received June 11, 2013; Accepted August 28, 2013)

ABSTRACT. Some N-acetyl pyrazoles including 1-(3-(3,4-dichlorophenyl)-5-(substituted phenyl)-4,5-dihydro-[1]*H*-pyrazole-1-yl) ethanones have been synthesised by solvent free cyclization cum acetylation of chalcones like substituted styryl 3,4-dichlorophenyl ketones using hydrazine hydrate and acetic anhydride in presence of catalytic amount of fly-ash: H_2SO_4 catalyst. The yield of these N-acetyl pyrazole derivatives are more than 75%. The synthesised N-acetyl pyrazoline derivatives were characterized by their physical constants and spectral data

Key words: Solvent-free cyclization cum acetylation, N-acetyl pyrazoles, IR, NMR spectra

INTRODUCTION

N-acetyl pyrazole is one of the derivatives of 4, 5-dihydro-[1]*H*-pyrazoles. These N-acetyl pyrazole derivatives are important precursor for the synthesis of some other pyrazoline based heterocycles such as cyanopyridine[1] indoxacarb[2] carbohydrazide hydrazine,[3] pyrimidine.[4] There are numerous solvent-free or solvent assisted acetylation methods available for the synthesis of N-acetylated pyrazoline derivatives in literature.[5–8] Glacial acetic acid and acetic anhydride were employed with solvent assisted conventional heating, solvent-free microwave and ultrasound wave irradiation for acetylation of pyrazolines.[5,6] The sulfated solid catalysts such as sulphated titania,[9] sulphated zirconia,[10] sulphated tinoxide[11], sulphated and molybdated iron oxide[12] and sulphated and phosphate zirconia[13] were employed for solvent assisted and solvent-free synthesis of organics. Osman et al.,[1] have synthesised 75% yield of 4,7-dimethoxy-5-(5-aryl-N-acetylpyrazolin-3-yl)benzofuran-6-ols by refluxing of Khellinone chalcones, hydrazine hydrate and glacial acetic acid. The 5-(*p*-tolyl)-4,5-dihydro-1-acetyl-pyrazol-3-yl-phenyl}-3H-quinazolin-4-ones were synthesised using refluxation method of corresponding chalcones with hydrazine acetic acid in ethanol by Mosaad et al.[14] More than 84% yield of some series of new N^1-cinnamoyl-3,5-diaryl-2-pyrazolines have been synthesised using microwave as well as conventional heating by Srivastava et al.[6] Shah et al., have synthesised 75% yield and studied the IR and ^{1}H NMR spectra of some new series of 4-(4-hydroxyphenyl)-3-chloro-1-{4-5-(substituted phenyl)-1-acetyl-4,5-dihydro-pyrazol-3-ylphenyl} azetidin-2-one with 3-chloro-1-{4-5-(substitutedphenyl)-4,5-dihydro-pyrazol-3-ylphenyl}-4-(4-hydroxyphenyl) azetidin-2-one in acetic acid.[15] N-acetyl-3-(2-naphthyl)-5-aryl pyrazoline derivatives were synthesised and studied their FTIR, NMR and HRMS data by Ethiraj et al.[16] Many N-acetyl pyrazole derivatives such as N-acetyl-3,5-diphenyl pyrazolines,[17] 1-acetyl-4-5-(3-chloro-4-fluorophenyl)-2-furyl-3-substituted phenyl-4,5-dihydro-1H-pyrazoles,[18] 2,4-bis-(tetrahydro-1,4-oxazine)-6-4"-{1"-acetyl-5"-(4"'-methoxyphenyl)-2"-pyrazoline-3"-yl} phenylamino-*s*-triazine[19], fluorine containing arylfuryl N-acetylpyrazolines 7 and 4,6-dimethoxy-5-(1-acetyl-5-aryl-2-pyrazolin-3-yl)benzobfurans[20] were synthesised by synthetic organic chemists using conventional heating method and studied their spectral data. These 1-acetyl pyrazoline derivatives possess important biological activities such as antibacterial,[6,7,15,18] endogenous proteolysis,[17] cytotoxicity,[16] EGFR kinase[8] and anti-inflammatory activities.[14] The literature survey reveals that there is no information available for solvent-free synthesis of some N-acetyl pyrazolines including 3-(3,4-dichlorophenyl)-5-(substitutedphenyl)-4,5-dihydro-[1]*H*-pyrazole) derivatives by cyclization of the respective chalcones and acetic anhydride in the presence of solid fly-ash:H_2SO_4 catalyst. Therefore the authors have taken efforts to synthesis some N-acetyl pyrazolines including 3-(3,4-dichlorophenyl)-5-(substitutedphenyl)-4,5-dihydro-[1]*H*-pyrazole) derivatives by solvent free microwave assisted cyclization of chalcones with hydrazine hydrate and acetic anhydride in presence of catalytic quantity of fly-ash:H_2SO_4. The purities of these pyrazolines were checked by their physical constants and spectral data with reference published earlier in literature.

EXPERIMENTAL

Materials and Methods

All chemicals used were procured from Sigma-Aldrich and E-Merck. Melting points of all pyrazoles have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000–400 cm^{-1}) have been recorded on BRUKER (Thermo Nicolet) Fourier transform spectrophotometer. The NMR spectra of all pyrazolines have been recorded on Bruker AV400 spectrometer operating at 400 MHz for recording ^{1}H and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Mass spectra have been recorded on SHIMADZU spectrometer using chemical ionization technique.

Preparation and Characterization of Fly-ash:H_2SO_4 Catalyst

The fly-ash:H_2SO_4 catalyst was prepared by the procedure published in literature.[21] In a 50 mL Borosil beaker, 1 g of Fly-ash and 0.8 mL (0.5 mol) of sulphuric acid were taken and mixed thoroughly with glass rod. This mixture was heated on a hot air oven at 85 °C for 1 h, cooled to room temperature, stored in a Borosil bottle and tightly capped. This was characterized by infrared spectra and SEM analysis.

Infrared spectral data of fly-ash:H_2SO_4 is ν(cm^{-1}): 3456 (OH); 3010 (C–H); 1495, 1390 (C–S); 1336, 1154 (S=O); and *op* modes: 1136, 1090, 976, 890, 850, 820, 667, 658, 620, 580, 498, 425.

The SEM images of pure Fly-ash and Fly-ash:H_2SO_4 at two different magnifications are shown in *Fig.* 1(a–d).

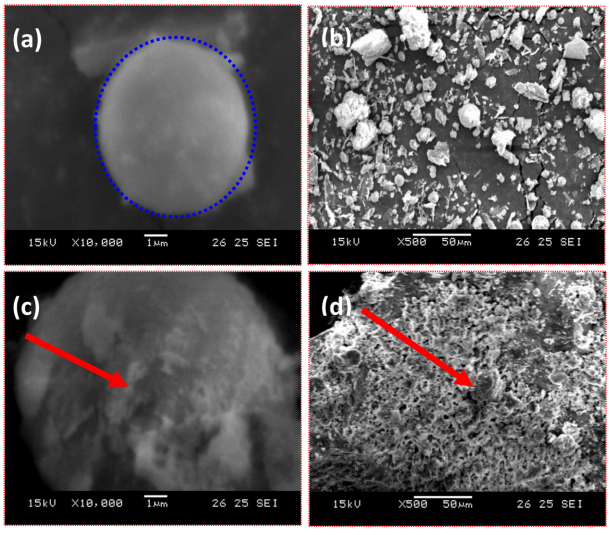


***Figure* 1.** SEM images of fly-ash:H_2SO_4 catalyst.

Figs. 1a and 1b depicted that the crystallinity is found to be more in pure fly ash. The spherical shaped particles are clearly seen at both magnifications in *Figs*. 1a and 1b. *Fig.* 1a reveals that the globular structure of pure fly ash (round shaped particle). This also seen from *Figs*. 1c and 1d that some of the particles are slightly corroded by H_2SO_4 (indicated by arrow mark) and this may be due to dissolution of Fly-ash by H_2SO_4. This will further confirmed by *Fig*. 1d, the well-shaped particles of pure Fly-ash. *Fig*. 1b is aggregated to *Fig.* 1d due to presence of H_2SO_4.

Synthesis of 3,4-Dichlorophenyl Chalcones[21]

The substituted styryl 3,4-dichlorophenyl ketones were synthesized by literature method. An appropriate equi-molar quantities of 3,4-dichloro acetophenone (2 mmol), substituted benzaldehydes (2 mmol) and Fly-ash:H_2SO_4 (0.5 g) were taken in Borosil tube and tightly capped. The mixture was subjected to microwave heated for 5–6 minutes (*Scheme* S1; See supplementary data) in a microwave oven at 480 W (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50 Hz, 2450 Hz, 100–750 W (IEC-705), and then cooled to room temperature. The organic layer was separated with dichloromethane and the solid product was obtained on evaporation. The solid, on recrystallization with benzene-hexane mixture gave glittering pale yellow solid. The insoluble catalyst was recycled by washing the solid reagent remained on the filter by ethyl acetate (8 mL) followed by drying in an oven at 100 °C for 1h and it was made reusable for further reactions. The purities of the synthesized chalcones were checked by their physical constants. The analytical, physical constants and mass fragments of the chalcones were presented in *Table* S1 (See supplementary data).

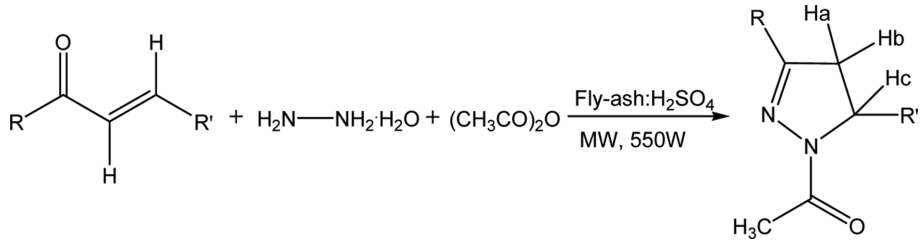
Synthesis of N-Acetyl Substituted Pyrazole Derivatives

An appropriate equi-molar quantities of chalcones (2 mmol), hydrazine hydrate (2 mmol), acetic anhydride (1 mmol) and fly-ash:H_2SO_4 (0.4 g) were taken in a 50 mL borosil beaker and closed with lid. The mixture was subjected to microwave irradiation for 4–6 minutes in a microwave oven at 550 watts, 2540 MHz frequency (*Scheme* 1) (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100–750W (IEC-705), and then cooled to room temperature. After separating the organic layer with dichloromethane, the solid product was separated by evaporation. The solid, on recrystallization from benzene-hexane mixture afforded glittering product. The insoluble catalyst was recovered by washing with ethyl acetate (8 mL) followed by drying in an oven at 100 °C for 1h and reused for

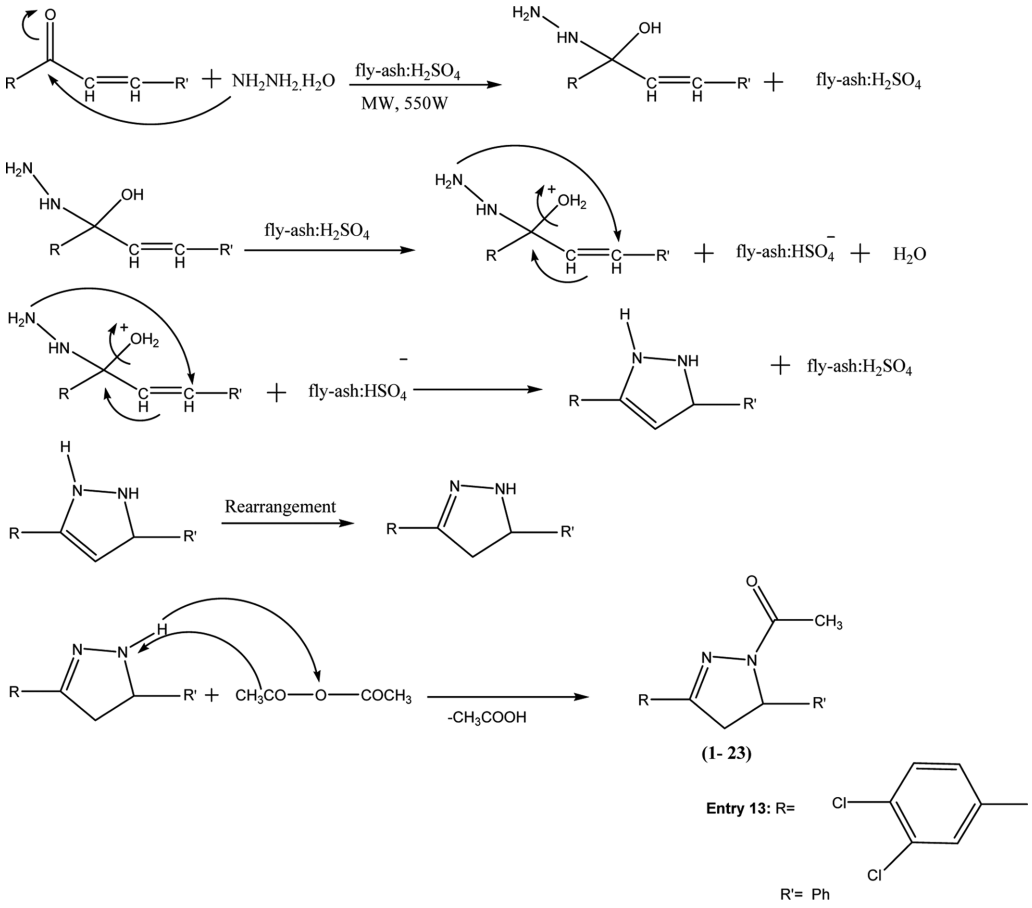
further reaction runs.

RESULTS AND DISCUSSION

In our organic chemistry research laboratory, we attempt to synthesize N-acetyl substituted pyrazoline derivatives by cyclization of chalcones possess electron with-drawing as well as electron donating group as substituents, hydrazine hydrate and acetic anhydride in the presence of acidic catalyst fly-ash:H_2SO_4 using microwave irradiation. Hence the authors have synthesized the N-acetyl substituted pyrazoline derivatives by the cyclization of 2 mmol of chalcone, 2 mmol of hydrazine hydrate and 1mmol of acetic anhydride under microwave irradiation with 0.4 g of fly-ash:H_2SO_4 catalyst at 550W for 4–6 minutes (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100–750W (IEC-705), (*Scheme* 1). During the course of this reaction fly-ash:H_2SO_4 catalyses cyclization cum acetylation between chalcones, hydrazine hydrate and acetic anhydride through elimination of water followed by proton transfer gave the



***Scheme* 1.** Synthesis of 1-acetyl pyrazoline derivatives synthesised by solvent-free cyclization cum acetylation of aryl chalcones with hydrazine hydrate and acetic anhydride in the presence of fly-ash:H_2SO_4 catalyst.



***Scheme* 2.** The proposed general mechanism for the synthesis of 1-acetyl pyrazoline derivatives by solvent-free cyclization cum acetylation of aryl chalcones with hydrazine hydrate and acetic anhydride in the presence of fly-ash:H_2SO_4 catalyst.

1-acetyl pyrazolines. The yield of the N-acetyl pyrazolines in this reaction is more than 75%. The proposed general mechanism of this reaction is shown in *Scheme* 2. In this cyclization and acetylation, first the amine nucleophilic attack of carbonyl carbon of the chalcone by nitrogen atom of hydrazine hydrate and the carbonyl oxygen gets hydroxylation. Another end of the nitrogen atom of hydrazine hydrate bonded with β-carbon of chalcone leads to cyclization, the unsaturation was shifted between carbonyl and α carbon of the chalcones. The hydroxylated group was eliminated as water molecule. Migration of proton of cyclic N-2 to 4th C of azole ring and the π-bond was shifted to N-2 and C-3 of the azole ring. The acetylation process was feasible by n-acetylation method. The chalcone containing electron donating substituent (OCH_3) gave higher yields than electron-withdrawing (halogens, NO_2) substituents. Further we have investigated this cyclization reaction with equimolar quantities of the styryl 3,4-dichlorophenyl ketone (entry 13), hydrazine hydrate and 1mole of acetic anhydride under the same condition as above. In this reaction the obtained yield was 90%. The effect of catalyst on this reaction was studied by varying the catalyst quantity from 0.1 to 1 g. As the catalyst quantity is increased from 0.1 to 0.4 g, the percentage of yield of product is increased from 82 to

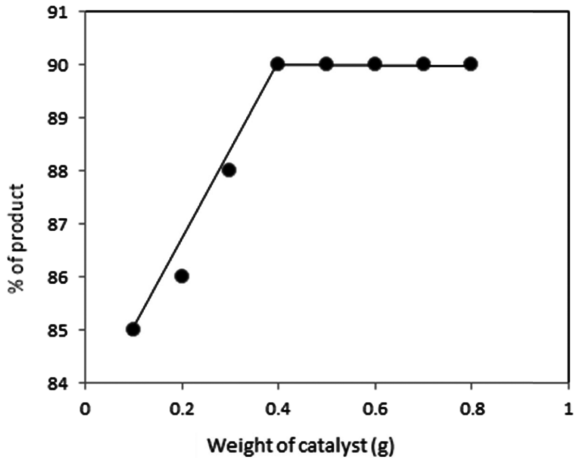


***Figure* 2.** The effect of catalyst loading.

***Table* 1.** The Analytical, physical constants and mass fragments (m/z) data of 1-acetyl pyrazoline derivatives synthesised by solvent-free cyclization cum acetylation of aryl chalcones with hydrazine hydrate and acetic anhydride in the presence of fly-ash:H_2SO_4 for the following reaction

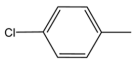
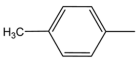
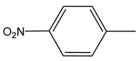
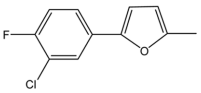
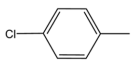
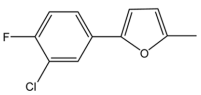
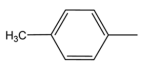
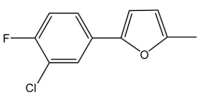
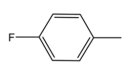
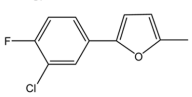
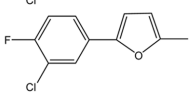
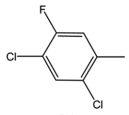
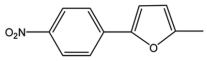
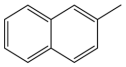
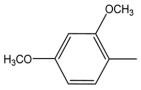
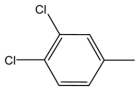
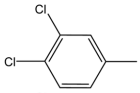
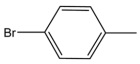
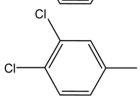
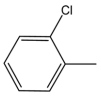
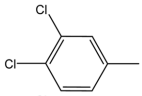
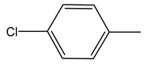
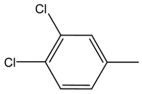
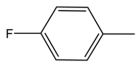
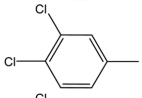
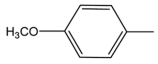
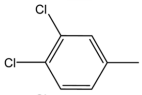
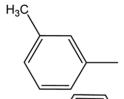
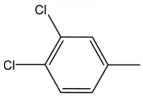
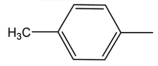
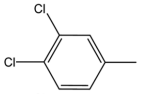
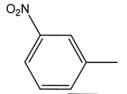
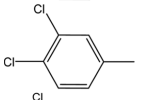
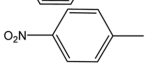
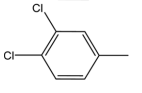
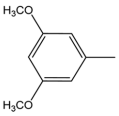
Entry	R	R′	M.W.	Yield (%)	m.p. (°C)	Mass (m/z)
1			264	77	123–124 (120–122)[17]	$264M^+$
2			298	89	111–112 (108–110)[17]	$298M^+$, $300M^{2+}$
3			278	89	109–110 (107–108)[17]	$278M^+$
4			309	85	163–164 (164–165)[17]	$309M^+$
5			382	85	167–168 (167)[18]	$382M^+$, $384M^{2+}$, $386M^{4+}$
6			418	85	177–178 (177)[18]	$418M^+$, $420M^{2+}$, $422M^{4+}$
7			398	88	172–173 (175)[18]	$398M^+$, $400M^{2+}$, $402M^{4+}$
8			402	86	173–174 (172)[18]	$402M^+$, $404M^{2+}$, $406M^{4+}$
9			398	86	163–134 (163)[18]	$398M^+$, $400M^{2+}$, $402M^{4+}$

***Table* 1.** Continued

Entry	R	R′	M.W.	Yield (%)	m.p. (°C)	Mass (m/z)
10			360	87	180–181 (178–180)[7]	$360M^{+}$, $362M^{2+}$, $364M^{4+}$
11			280	85	136–137 (136)[6]	$280M^{+}$
12			404	89	154–155 (152–155)[16]	$404M^{+}$
13			334	90	121–122	$334M^{+}$, $336M^{2+}$, $338M^{4+}$
14			412	85	135–36	$412M^{+}$, $414M^{2+}$, $416M^{4+}$
15			368	85	119–120	$368M^{+}$, $370M^{2+}$, $372M^{4+}$
16			368	86	131–132	$368M^{+}$, $370M^{2+}$, $372M^{4+}$
17			350	87	147–148	$350M^{+}$, $352M^{2+}$, $354M^{4+}$
18			364	91	112–113	$364M^{+}$, $366M^{2+}$, $368M^{4+}$
19			348	90	125–126	$348M^{+}$, $350M^{2+}$, $352M^{4+}$
20			348	89	116–117	$348M^{+}$, $350M^{2+}$, $352M^{4+}$
21			378	85	152–153	$378M^{+}$, $380M^{2+}$, $382M^{4+}$
22			378	85	147–148	$378M^{+}$, $380M^{2+}$, $382M^{4+}$
23			394	89	121–122	$394M^{+}$, $396M^{2+}$, $398M^{4+}$

90%. Further increase in the catalyst amount beyond 0.4 g, there is no significant increase in the percentage of the product. The effect of catalyst loading is shown in *Fig*. 2. The optimum quantity of catalyst loading was found to be 0.4 g. The results, analytical and mass spectral data are summarized in *Table* 1. The mass spectra and the possible fragments of the selective 1-acetyl pyrazolines are presented in

***Table* 2.** Reusability of fly-ash:H_2SO_4 catalyst on cyclization cum acetylation of styryl 3,4-dichlorophenyl ketone (2 mmol) with hydrazine hydrate (2 mmol) and acetic anhydride (1 mmol) under microwave irradiation (entry 13)

Run	1	2	3	4	5
Yield	90	90	89.5	89.5	89

***Table* 3.** The effect of solvents in conventional heating and without solvent in microwave irradiation on yield of 1-acetyl pyrazoline (entry 13)

Solvents												Microwave irradiation		
MeOH			EtOH			DCM			THF					
FA	SA	FASA	FA	SA	FASA	FA	SA	FASA	FA	SA	FAPA	FA	SA	FASA
72	13	78	70	15	85	74	12	85	75	16	87	80	23	90

MeOH=Methanol; EtOH=Ethanol; DCM= Dichloromethane; THF=Tetrahydrofuran; FA=fly-ash; SA=Sulphuric acid; FASA=fly-ash:H_2SO_4

***Table* 4.** The infrared, NMR spectral data of 1-(3-(3,4-dichlorophenyl)-5-(substitutedphenyl)-4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones (entries 13–23)

Entry	X	IR		^{1}H NMR					^{13}C			
		C=N	C=O	H_a	H_b	H_c	CH_3	X	C=N	C=O	CH_3	X
13	H	1574.18	1641.20	3.297	3.819	5.568	2.934	–	159.06	168.67	24.46	–
14	4-Br	1578.21	1644.65	3.197	3.857	5.565	2.401	–	159.66	173.56	24.61	–
15	2-Cl	1576.84	1643.82	3.195	3.879	5.594	2.295	–	158.97	172.96	25.87	–
16	4-Cl	1577.71	1647.41	3.851	2.996	5.671	2.265	–	158.67	169.80	25.81	–
17	4-F	1576.21	1644.17	3.201	3.846	6.071	2.401	–	159.71	168.12	24.16	–
18	4-OCH_3	1570.07	1638.74	3.117	3.701	5.457	2.249	3.845	158.58	168.80	22.74	58.45
19	3-CH_3	1571.19	1640.94	3.153	3.794	5.497	2.310	2.401	157.67	172.05	24.77	24.68
20	4-CH_3	1570.27	1639.71	3.167	3.807	5.943	2.287	2.316	158.09	171.94	23.79	24.35
21	3-NO_2	1575.16	1644.97	3.208	3.943	5.973	2.441	–	159.87	174.91	26.97	–
22	4-NO_2	1575.97	1645.08	3.217	3.997	5.997	2.531	–	159.97	174.96	26.87	–
23	3,5-$(OCH_3)_2$	1572.61	1640.40	3.071	3.671	5.471	2.031	–	158.08	173.17	26.71	–

supplementary data (See supplementary data). The reusability of this catalyst was studied for the cyclization of styryl 3,4-dichlorophenyl ketone, hydrazine hydrate and acetic anhydride (entry 13) and is presented in *Table* 2. From the *Table* 2, first two runs gave 90% product. The third, fourth and fifth runs of reactions gave respectively the yields 89.5%, 89.5% and 89% of 1-acetyl pyrazolines. There was no appreciable loss in its effect of catalytic activity observed up to fifth run. The effect of solvents on the yield was also studied with methanol, ethanol, dichloromethane and tetrahydrofuran from each component of the catalyst (entry 13). Similarly the effect of microwave irradiation was studied on each component of the catalyst. The effect of solvents on the yield of 1-acetyl pyrazolines was presented in *Table* 3. From the table highest yield of 1-acetyl pyrazolines obtained from the cyclization cum acetylation of chalcone, hydrazine hydrate and acetic anhydride with the catalyst fly-ash:H_2SO_4 in microwave irradiation. The infrared and nmr spectroscopic data of these 1-acetyl pyrazolines are summarized in *Table* 4.

CONCLUSION

A series of some 1-acetyl pyrazolines including 1-(3-(3,4-dichlorophenyl)-5-(substituted phenyl)-4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones have been synthesised by microwave assisted fly-ash:H_2SO_4 catalyzed solvent free cyclization of chalcones cum acetylation of pyrazole and acetic anhydride. The yield of the synthesized 1-acetyl pyrazolines are more than 75%. This methodology offers efficient, solvent free cum acetylation of chalcones and non-hazardousness to the environment.

Acknowledgments. The publication cost of this paper was supported by the Korean Chemical Society.

REFERENCES

1. Osman, S. A.; Yosef, H. A. A.; Hafez, T. S.; Sawy, A. A. E.; Mousa, H. A.; Hassan, A. S. *Aust. J. Basic Appl. Sci*. **2012**, *6*, 852.
2. Zhao, P. L.; Wang, F.; Zhang, M. Z.; Liu, Z. M.; Huang, W.; Yang, G. F. *J. Agric. Foodchem*. **2008**, *56*, 10767.
3. Yusuf, M.; Jain, P. *Arab. J. Chem*. **2011**. DOI:10.1016/j.arabjc.2011.09.013.
4. Mistry, R. N.; Desai, K. R. *E. J. Chem*. **2005**, *2*, 30.
5. Kanagarajan, V.; Ezhilarasi, M. R.; Gopalakrishnan, M. *Spectrochim. Acta* **2011**, *78A*, 635.
6. Srivastava, Y. K.; Malhotra, G.; Gothwal, P. *Rasayan J. Chem*. **2010**, *3*, 584.
7. Holla, B. S.; Shivananda, M. K.; Akberali, P. M.; Shenoy, M. S. *Indian J. Chem*. **2000**, *39B*, 440.
8. Lv, P. C.; Li, H. Q.; Sun, J.; Zhou, Y.; Zhu, H. L. *Bioorg. Med. Chem*. **2010**, *18*, 4606.
9. Krishnakumar, B.; Velmurugan, R.; Swaminathan, M. *Catal. Commun*. **2011**, *12*, 375.

10. Reddy, B. M.; Sreekanth, P. M.; Lakshmanan, P. *J. Mol. Catal. A: Chem*. **2005**, *237*, 93.
11. Kafuku, G.; Lee, K. T.; Mbarawa, M. *Chem. Papers* **2010**, *64*, 734.
12. Trewhella, M. J.; Grint, A. *Fuel* **1987**, *66*, 1315.
13. Stojkovic, N.; Vasic, M.; Marinkovic, M.; Randjelovic, M.; Purenovic, M.; Putanov, P.; Zarubica. A. *Chem. Ind. Chem. Eng. Quart*. **2012**, *18*, 209.
14. Mosaad, M. S.; Mohsen, K. M.; Emad, K. M. M.; Abotaleb, N.; Salwa, N. M.; Marwa, A. F. *Acta Poloniae Pharm.-Drug Res.* **2010**, *67*, 159.
15. Shah, S. H.; Patel, P. S. *Int. J. Chem. Tech. Res*. **2012**, *4*, 933.
16. Ethiraj, K. R.; Nithya, P.; Krishnakumar, V.; Jesil Mahew, A.; Nawaz Khan, F. *Res. Chem. Intermed.* **2012**. DOI: 10.1007/s11164-012-0718-3.
17. Singh, M.; Raghav, N. *Int. J. Pharm. Pharm. Sci*. **2013**, *5*, 80.
18. Rana, A. K.; Lade, S. B.; Sorathia, S.; Joshi, M. J.; Shah, N. M. *Der Chim. Sinica*. **2012**, *3*, 965.
19. Solankee, A.; Patel, R.; Patel, K. *Der Chim. Sinica*. **2011**, *3*, 317.
20. Abdel Hafez, O. M.; Ahmed, Kh. M.; Haggag, E. E. *Molecules* **2001**, *6*, 396.
21. Thirunarayanan, G.; Mayavel, P.; Thirumurthy, K. *Spectrochim Acta* **2012**, *91A*, 18.
22. Thirunarayanan, G.; Surya, S.; Srinivasan, S.; Vanangamudi, G.; Sathiyendiran, V. *Spectrochim. Acta, Part A.* **2010**, *75*, 152.
23. Thirunarayanan, G. *Iup. J. Chem*. **2012**, *5*, 41.
24. Thirunarayanan, G.; Thirumurthy, K.; Vanangamudi, G.; Subramanian, M.; Arulkumaran, R.; Kamalakkannan, D.; Sundararajan, R.; Sakthinathan, S. P.; Vijayakumar, S.; Ranganathan, K.; Suresh R. *Elixir Org. Chem*. **2012**, *45*, 7898.
25. Sathiyamoorthi, K.; Mala, V.; Suresh, R.; Sakthinathan, S. P.; Kamalakkannan, D.; Ranganathan, K.; Arulkumaran, R.; Sundararajan, R.; Vijayakumar, S.; Vanangamudi, G.; Thirunarayanan, G. *Int. Lett. Chem. Phys. Astro.* **2013**, *7*(2), 102.