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Tungstic Acid Catalyzed Four Components One Pot Synthesis of Pyranopyrazole in Non-Aqueous Solvent

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***Abstract*-- An efficient, fast and facile route for one pot microwave synthesis of pyranopyrazole derivatives through the condensation of aromatic aldehyde, ethyl acetoacetate, malononitrile, and hydrazine hydrate by using tungstic acid catalyst. The reaction is proceeding through tungstic acid catalyzed Knoevenagel condensation, Michael addition and intermolecular cyclisation. The important aspects of the present methodology very fast.**

***Keyword*- tungstic acid, pyranopyrazole, cyclocondensation**

I. Introduction

Pyranopyrazole are fused heterocyclic compound, which are important because of their biological properties such as antifungal, antibacterial, vasodilator activities and anticancer agent.[1] pyranopyrazole are also useful for the antifungicidal, agrochemical, moluscidal, and furthermore some of these compounds are commonly in employment such as cosmetics and pigment.[2]

Pyranopyrazole were first obtained by reaction between 3-methyl 1-phenyl pyrazole-5-one and tetracynomethylene.[3] The 2-amino 4-substituted pyrano (2, 3-c) pyrazole 3-carbonitrile were obtained in 1974 by addition of malononitrile on 4-arylidine 2-pyrazolin-5-one.[4] Afterwards several other synthetic approaches to synthesize of these compound were reported, those compound include one pot four component cyclocondensation reaction of aldehyde, ethyl acetoacetate , malononitrile and hydrazine hydrate.[5,6]

Multicomponent reactions (MCRs) are more convenient than multistep reaction. MCR came into light over routine multistep synthesis counterpart owing to their atom economy, energy efficiency, lower cost, short reaction time, environmentally friendly nature and simple purification technique. Hence nowadays heterocyclic compound was synthesized by MCR method.[7,8]

Pyranopyrazole synthesis are some different catalyst are reported like L-proline,[9] MgO,[10] bleaching earth clay,[11] sodium benzoate,[12] CTACl,[13] piperidine,[14] ammonium chloride,[15] glycine,[16] meglumine[17] and 6-amino β-cyclodextrine.[18]

But above catalyst are required high energy, more time and catalyst are hazardous to human health, therefore required fast method for synthesis of pyranopyrazole. Here report one pot four component synthesis of pyranopyrazole by using tungstic acid is heterogeneous catalyst in organic solvent.

Tungstic acid is a hydrated form of tungstic trioxide, WO_3, [19-20] Tungstic acid has been used to catalysed few organic reactions such as oxidation of cyclohaxanone, synthesis of 3, 3-bis(1*H*-indo-3yl) indolin-2-one [21], hydroxylation of olefin and epoxidation of olefin.[22]

Considering the above facts, we have developed an efficienct methodology for one pot four componant synthesis of pyranopyrazole by using heterogenous catalyst, tugnstic acid.

II. Result And Discussion

Here we report tungstic acid catalyzed one pot four component synthesis of pyranopyrazole from aromatic aldehyde, ethyl acetoacetate, malononitrile and hydrazine hydrate.

In order to best experimental conditions, we have considered reaction of benzaldehyde, malononitrile, ethyl acetoacetate and hydrazine hydrate in presence of tungstic acid under microwave as model reaction to get product **(5a).**

Model reactions was screen with different solvent like ethanol (EtOH), methanol (MeOH), acetonitrile (ACN), dichloromethane (DCM), dimethylformamide (DMF), formation of product in all solvent **(Table-1 entry 1-5).** After screening of the solvent, ethanol has higher yield as compare to other solvent (**Table 1-entry 1).** Also screen the solvent of aqueous ethanol and aqueous methanol **(Table 1 entry 6-7),** reaction precede in both solvent but lesser yield compare to ethanol. Therefore model reactions were selected with ethanol for further reactions.

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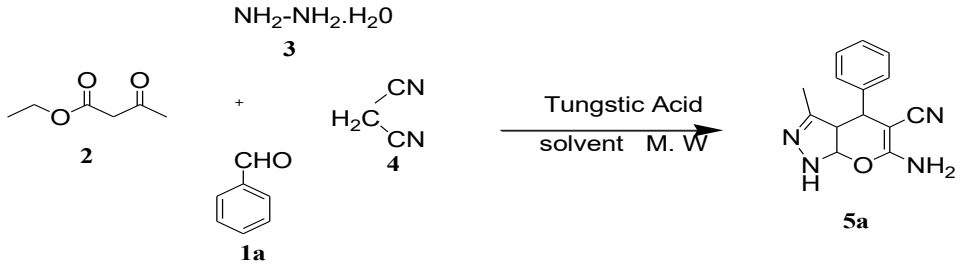


Scheme-1

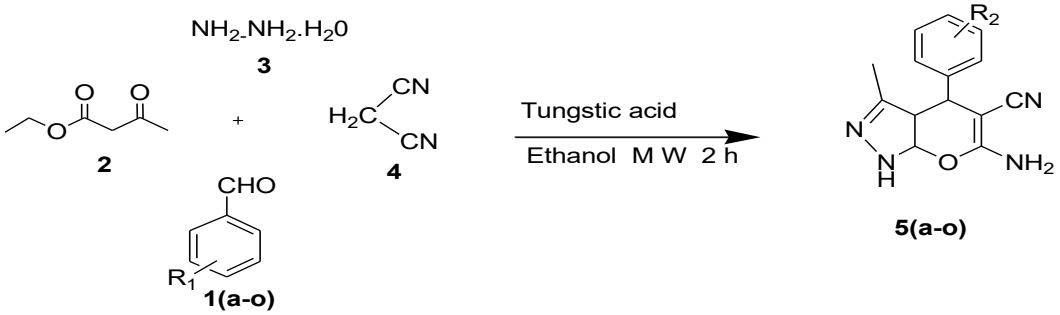
Table-1
Screening of solvent on four component one pot synthesis of pyranopyrazole

S.N	Solvent	Time (h)	Yield[b] (%)
1	Ethanol	2	84
2	Methanol	2	82
3	Acetonitrile	2	56
4	DCM	2	50
5	DMF	2	-
6	Ethanol+ water	2	75
7	Methanol + water	2	75

[a]Reaction condition – aromatic aldehyde (5 mmol), malononitrile (5 mmol), hydrazine hydrate (5 mmol) and ethyl acetoacetate (5 mmol) in solvent(15 mL) with tungstic acid (5 mmol) in microwave at 2 h. [b] isolated yield

Aromatic aldehyde with substitution on ortho, meta, and para position with electron donating as well as electron withdrawing group has been successfully formation desire product. Starting from substitution on para position of aldehyde with chloro, nitro, fluro, hydroxy, methoxy, methyl, N, N dimethyl group to give product.

(**Table 2, entry 2-9)** then ortho position of aldehyde with chloro and hydroxy group to give product. **(Table 2 entry 10-11)** Then meta nitro benzaldehyde to give product. **(Table 2 entry 12)** finally taken heterocyclic aldehyde for this reaction surprisingly to give desire product. **(Table 2 Entry 13-15)**



Scheme-2

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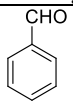
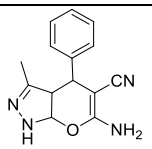
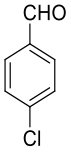
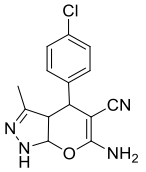
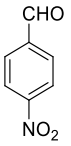
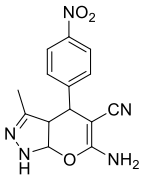
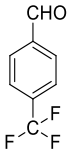
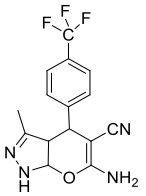
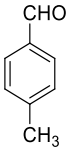
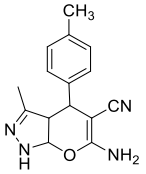
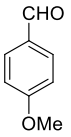
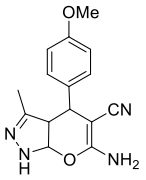
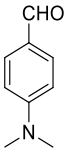
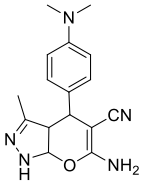
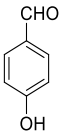
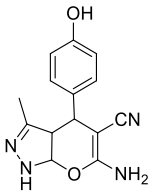
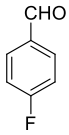
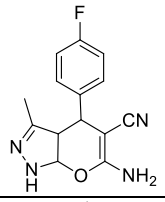
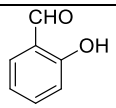
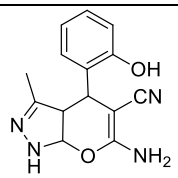
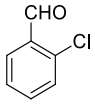
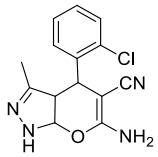
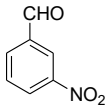
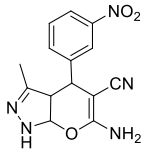
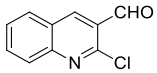
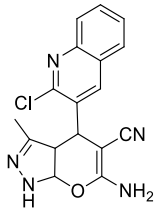
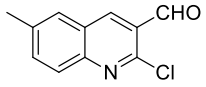
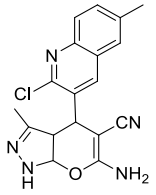
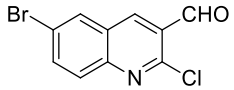
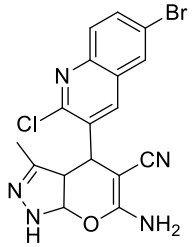
Table-2
Tungstic acid catalyzed one pot four components synthesis of pyranopyrazoles

S.N.	Aldehyde	Product	product code	Yield (%)
1			5a	84
2			5b	88
3			5c	80
4			5d	76
5			5e	78
6			5f	82
7			5g	76
8			5h	68

9			5i	70
10			5j	72
11			5k	76
12			5l	80
13			5m	78
14			5n	78
15			5o	76

[a]Reaction condition – aromatic aldehyde (5 mmol), malononitrile (5 mmol), hydrazine hydrate (5 mmol) and ethyl acetoacetate (5 mmol) in ethanol (15 mL) with tungstic acid (5 nmol) in microave at 2 h. [b] isolated yield. [c]Products were characterized by comparing their physical constant, ^{1}HNMR, ^{13}CNMR data in literature.

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III. Conclusion

In summary, we have used solid acid catalyst for the one pot synthesis of pyronopyrazole The developed protocol is an efficient, eco-friendly and catalyst tungstic acid is reusable

IV. Experimental

4.1 General

All chemicals purchased from commercial suppliers. FTIR data (KBr pallets) was taken on a SIMADZU IR Spectrophotometer, ^{1}H NMR and ^{13}C NMR Spectra were recorded on Bucker Avance II 400MHz spectrometer at ambient temperatures in $CDCl_3$ as solvent. Mass spectrums were recorded using JMS-T100LC, Accu TOF in acetonitrile solvent. Thin Layer chromatography was carried out using aluminium backed plates precoated with silica gel 60 were visualized by quenching of UV fluorescence.

4.2 General procedure for synthesis of pyranopyrazole

A mixture of benzaldehyde (5 mmol), malononitrile (5 mmol), hydrazine hydrate (5 mmol) and ethyl acetoacetate (5 mmol) was dissolved in ethanol (15 mL) containing microwave cuvate then add tungstic acid Reaction mixture was run under microwave and progress of reaction checked by using thin layer chromatography in solvent system pet ether: ethyl acetate (3: 1). After completion of reaction (2 h), reaction mixture was filtered using silica bed to remove the catalyst and washed it with ethanol (50 mL). The reaction mixture was concentrated by using rotary evaporated under vacuum and obtained crude products. The purification is done by using recrystallization in ethanol solvent.

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