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$B(C_6F_5)_3$ catalyzed one-pot three-component Biginelli reaction: An efficient and environmentally benign protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones

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Abstract. *Tris*(pentafluorophenyl)borane catalyzed, one-pot, simple, efficient and environmentally benign protocol for the synthesis of dihydropyrimidinones/thiones *via* Biginelli reaction has been described. The main highlights of the present protocol is low catalyst loading, low toxicity, compatibility with acid-labile-protecting groups, short reaction time, consistently excellent yields and simple reaction/workup procedure. Moreover, the applicability of the present methodology for large-scale synthesis of monastrol highlights its potential for bulk synthesis.

Keywords. Biginelli reaction; *Tris*(pentafluorophenyl)borane; multicomponent reaction; dihydropyrimidinone; dihydropyrimidinthione.

1. Introduction

The Biginelli reaction is inarguably one of the most useful multi-component reactions that involves the condensation between aldehydes and β-dicarbonyl compounds with urea or thiourea to give 3,4-dihydropyrimidin-2-(1*H*)-ones (DHPMs) and their thione analogues.[1] The original reaction was first reported by the Italian chemist Pietro Biginelli in 1893 and was catalyzed by mineral acids.[2]

In recent decades, dihydropyrimidinones and its derivatives gained prominence in organic and medicinal chemistry because of their versatile pharmacophoric features, as compounds with this scaffold exhibit a broad range of biological activities such as calcium channel modulator, anti-hypertensive, anti-viral, anti-oxidant, anti-bacterial, anti-inflammatory agents, neuropeptide Y (NPY) antagonist, and α_{1a}-adrenergic antagonist.[3] Monastrol is the only cell-permeable molecule currently known as a specific inhibitor of mitotic kinesin Eg5 and is considered as lead molecule for the development of new anti-cancer agents.[4a,b] Also, SQ 32926 and SQ 32547 have been identified as a potent orally active antihypertensive agents.[4c,d] Moreover, several natural alkaloids, such as batzelladine[4e] and crambine[4f] containing the dihydropyrimidine core unit, isolated from marine sources were found to be potent HIV gp-120-CD4 inhibitors.

The outstanding outcome of dihydropyrimidinones/thiones motifs as pharmacologically active compounds has contributed towards Biginelli cyclocondensation applications in drug industries.[4g,h] The expansion of natural products chemistry with structural diversification of dihydropyrimidinone motif also found synthetic attention from Biginelli reaction. Therefore, there has been continuous interest from organic and medicinal chemists towards the development of milder and more efficient methodologies for the synthesis of this class of compounds. A variety of methods for promoting the Biginelli reaction employing reagents and catalysts such as $NaHSO_4/SiO_2$,[5a] NH_2SO_3H,[5b] 12-molybdophosphoric acid,[5c] $KHSO_4$[5d] trifluoromethanesulfonate,[5e] $Fe(HSO_4)_3$,[5f] $Yb(OTf)_3$,[5g] $Mn(OAc)_3$,[5h] $BF_3{\cdot}Et_2O$,[5i] Yb(III)-resin,[5j] sulfated zirconia,[5k] Al_2O_3,[5l] $Bi(OTf)_3$,[6a] $TaBr_5$,[6b] $Cu(OTf)_2$,[6c] $Ce(NO_3)_3{\cdot}6H_2O$,[6d] SmI_2,[6e] $ZrOCl_2{\cdot}8H_2O$,[6f] $ZrCl_4$,[6g] $Sr(OTf)_2$,[6h] $InCl_3$,[6i] $H_4PMo_{11}VO_{40}$,[7a] $H_3PW_{12}O_{40}/SiO_2$,[7b] Dowex-50W,[7c] CaF_2,[7d] Fe_3O_4 nanoparticles,[7e] sulfonated β-cyclodextrine,[7f] hexaaquaaluminium(III) tetrafluoroborate,[7g] zeolite[7h] and polyoxometalate[7i] have been developed. Many other synthetic approaches including combinatorial approach,[8a] microwave,[8b] sonication,[8c] ionic liquids[8d] and organocatalysts[8e] have been actively pursued for the preparation of Biginelli products. Very recently, $Fe(OTs)_3{\cdot}6H_2O$,[9a] piperazine/TMSCl,[9b] I_2,[9c]

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nanomagnetic-supported sulfonic acid,[9d] and Q-tube[9e] have also been utilized for the synthesis of 3,4-dihydropyrimidinones/thiones. However, some of the reported protocols suffer from various disadvantages such as high catalyst loading, strong acidic conditions, incompatibility with acid-sensitive protecting groups, low yield, high temperature, prolonged reaction times, cumbersome methodology, eco-hazards and complexity in product isolation.

In continuation with our interest in developing novel synthetic methodologies, we report an efficient and environmentally benign protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones using catalytic amount of *tris*(pentafluorophenyl)borane as a convenient and non-conventional Lewis acid. *Tris*(pentafluorophenyl)borane is gaining importance due to its availability, less toxicity, thermal stability and water-tolerant nature.[10a] In recent years, the potential utility of $B(C_6F_5)_3$ was explored by several researchers in various organic transformations such as Friedel-Crafts alkylation of activated arenes,[10b] regio- and stereo-selective cyclizations of unsaturated alkoxysilanes,[10c] polymethylhydrosiloxane (PMHS) activation for reduction of different functional groups.[10d,e] $B(C_6F_5)_3$ was also employed in the reduction of imines,[11a] Ferrier azaglycosylation,[11b] epoxide ring opening[11c] and reduction of alcohols with silane.[11d] $B(C_6F_5)_3$ was also used for the multi-component synthesis of 1,8-dioxodecahydroacridines and α-amino nitriles.[12] Very recently, we also reported an efficient protocol for the synthesis of 5-substituted 1*H*-tetrazoles *via* [3+2] cyclo-addition, acylation reactions and one-pot oxidative esterification of aldehydes to carboxylic esters using $B(C_6F_5)_3$.[13] To the best of our knowledge, this is the first demonstration of $B(C_6F_5)_3$ promoted one-pot Biginelli cyclocondensation reaction.

2. Experimental

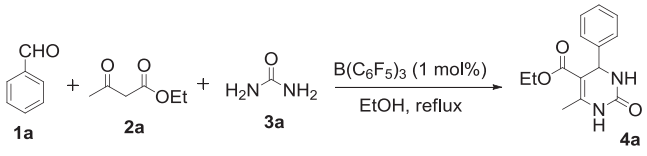
2.1 *General experimental procedure for the synthesis of dihydropyrimidinones*

A mixture of benzaldehyde **1a** (106 mg, 1 mmol), ethyl acetoacetate **2a** (130 mg, 1 mmol) and urea **3a** (90 mg, 1.5 mmol) in EtOH (10 mL) was refluxed in the presence of $B(C_6F_5)_3$ (18.1 mg, 1 mol%). After completion of reaction, as indicated by TLC analysis, the solvent was evaporated. The resulting mass was treated with ice-cold water and the solid obtained was filtered, washed with cold water, dried and re-crystallized from ethanol to give pure product (**4a**).

3. Results and Discussion

To evaluate the feasibility of using *tris*(pentafluorophenyl)borane [B(C6F5)3] as a catalyst in the Biginelli reaction, a model reaction (scheme 1) utilizing building blocks such as benzaldehyde (**1a**) ethyl acetoacetate (**2a**) and urea (**3a**) to get 5-ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**4a**), the reactions were performed under various reaction conditions and the results are summarized in table 1. The reaction of **1a**, **2a** and **3a** in EtOH was first tested in the presence of 0.5 mol% of $B(C_6F_5)_3$, the desired product **4a** was obtained in 76% yield after 4 h (table 1, entry 1). Next, optimization of reaction conditions was undertaken to increase the yield of the product using different amounts of $B(C_6F_5)_3$. Interestingly, the yield of **4a** was significantly increased to 95% by employing 1 mol% of the catalyst (table 1, entry 2). Further improvement was not observed in terms of either reaction time or yield on increasing the amount of catalyst (table 1, entry 3). On the basis of these results, 1 mol% of $B(C_6F_5)_3$ was considered to be the optimum concentration of catalyst for this reaction. In the absence of a catalyst, only 15% yield of the desired product was acquired even after longer reaction time (table 1, entry 4). The reaction was also executed under solvent-free conditions and afforded desired product in 70% yield after 5 h (table 1, entry 5). Furthermore, the catalytic efficiency of $B(C_6F_5)_3$ was examined using different solvents, which showed prominent influence on reaction time and yields to obtain desired products (table 1, entries 6–9). Water, THF and toluene were not found to be suitable solvents for the reaction; however excellent yield of the desired product was obtained using CH_3CN, although longer reaction time was required for the completion of reaction (table 1, entry 9). Among the solvents tested, EtOH was chosen as the best solvent with consideration to the reaction time, yields and environmental impact. Consequently, 1 mol% of $B(C_6F_5)_3$ and EtOH as solvent were selected as the optimized reaction parameters for the synthesis of respective dihydropyrimidinones/thiones (table 1, entry 2).

To establish the generality and scope of present methodology, various aromatic and heteroaromatic



Scheme 1. $B(C_6F_5)_3$ catalyzed synthesis of dihydropyrimidinone **4a**.

Table 1. Optimization of reaction conditions for the synthesis of dihydropyrimidinone **4a**[a].

Entry	$B(C_6F_5)_3$ (mol%)	Solvent	Time (h)	Yield[b] (%)
1	0.5	EtOH	4	76
2	1	EtOH	2.5	95
3	5	EtOH	2.5	95
4	-	EtOH	12	15
5[c]	1	Neat	5	70
6	1	Water	6	47
7	1	THF	6	76
8	1	Toluene	6	67
9	1	CH_3CN	3.5	92

[a]Reaction conditions: Benzaldehyde (**1a**, 1 mmol), ethyl acetoacetate (**2a**, 1 mmol), urea (**3a**, 1.5 mmol), reflux. [b]Isolated yield. [c]Reaction was performed under solvent-free conditions.

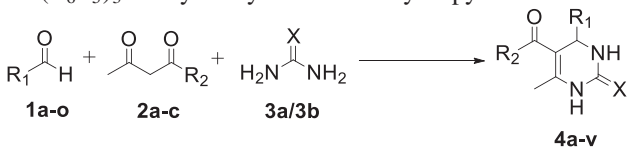
aldehydes (**1a-o**) were treated with urea or thiourea (**3a/3b**) and 1,3-dicarbonyl compounds (**2a-c**) under optimized reaction conditions to afford corresponding dihydropyrimidinones/thiones and the results are summarized in table 2.

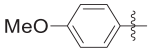
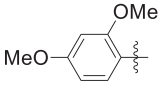
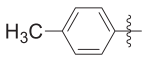
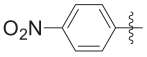
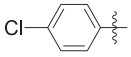
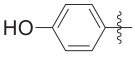
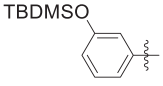
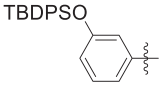
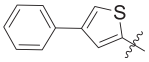
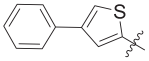
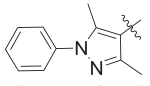
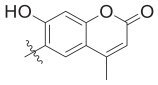
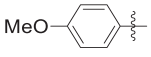
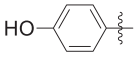
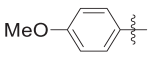
It was observed that the compounds containing both electron-withdrawing and electron-donating substituents on aromatic ring reacted efficiently under the present reaction conditions to obtain corresponding 3,4-dihydropyrimidin-2(1*H*)-ones/thiones (**4a-h,4q,4r**) in excellent yields and high purity; however, *ortho*-substituted aromatic aldehydes (**1c,1g**) required longer reaction time to achieve desired products in high yields. To check the compatibility and mildness of the present reaction conditions, the reactions were carried out using aromatic aldehydes tethered with acid-sensitive protecting groups (**1i,1j**) under similar reaction conditions. It is noteworthy that acid-sensitive protecting groups such as TBDMS and TBDPS were unaffected and high yields of products (**4i,4j**) were obtained. The novel aspect of the present methodology was successfully extended to various heterocycles, which proceeded smoothly to afford the corresponding dihydropyrimidinones (**4k-o**) in good to excellent yields. However, heterocyclic aldehydes reacted relatively, in a sluggish manner, as compared to aromatic aldehydes. The yield of the desired products dropped significantly in case of 3,5-dimethyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**1n**) and 7-hydroxy-4-methyl-2-oxo-2*H*-chromene-6 carbaldehyde (**1o**). To generalize the catalytic efficiency of $B(C_6F_5)_3$ for the Biginelli reaction, we employed thiourea (**3b**) instead of urea (**3a**) under similar reaction conditions and obtained corresponding 3,4-dihydropyrimidin-(2*H*)-thiones (**4p-s**) in high yields, which are also of much interest with regard to biological activity. Comparatively, thiourea (**3b**) was found to be more reactive than urea (**3a**) (table 2, entry 1 vs. 16, entry 2 vs. 17 and entry 8 vs. 18). We further investigated the scope of the present protocol by replacing β-keto ester (**2a**) with β-diketone (**2c**). Notably, β-keto ester **2a** exhibited better reactivity over the β-diketone **2c** (entry 1 vs. 20, entry 2 vs. 22 and entry 11 vs. 21). The results mentioned earlier clearly indicate the generality and scope of the present methodology for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones expeditiously using a wide range of substrates. The notable features of this methodology are; mild reaction conditions, cleaner reaction, low catalyst loading, simple experimental and isolation procedures as well as tolerance of varied functional groups such as TBDMS, TBDPS, alkoxy, hydroxyl, nitro, chloro, bromo and nitrile under the present reaction conditions, which makes it a useful and attractive process for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones.

Encouraged by the results mentioned above, we next examined the feasibility of the present protocol to synthesize biologically important molecule such as monastrol (mitotic kinesin Eg5 inhibitors) in large scale. On large-scale operation, the reaction of 3-hydroxy benzaldehyde (**1w**) (5 g, 1 equiv.) with equimolar amounts of ethyl acetoacetate (**2a**) (5.3 g, 1 equiv.) and thiourea (**3b**) (4.6 g, 1.5 equiv.) by employing (0.74 g, 1 mol%) of $B(C_6F_5)_3$ in EtOH (40 mL) was refluxed for 3 h to achieve monastrol in 88% yield with 96.7% purity (scheme 2).

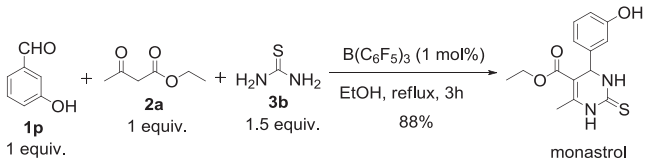
Presumably, the reaction may proceed *via* formation of acyl imine intermediate (**6**) formed by the reaction of aldehyde and urea, which is activated by co-ordination of $B(C_6F_5)_3$ (key and rate-limiting step) and undergoes subsequent nucleophilic attack by the active methylene carbon of the β-dicarbonyl compounds through its enol form to produce open chain ureide (**8**), followed by

Table 2. $B(C_6F_5)_3$ catalyzed synthesis of dihydropyrimidinones and thiones[a–c].

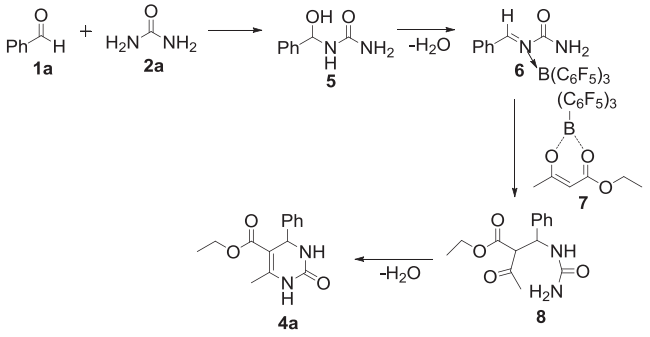


Entry	R_1	R_2	X	Time (h)	Product	Yield[d] (%)	Ref.
1		OEt	O	3	**4a**	95	1a
2		OEt	O	3	**4b**	97	1a
3		OEt	O	4.5	**4c**	94	5l
4		OEt	O	3	**4d**	95	6e
5		OEt	O	3	**4e**	96	5j
6		OEt	O	3	**4f**	94	8d
7		OEt	O	4	**4g**	92	5h
8		OMe	O	4.5	**4h**	93	9c
9[e]		OMe	O	4	**4i**	95	-
10[e]		OEt	O	4.5	**4j**	91	-
11		OEt	O	4	**4k**	95	7i
12[e]		OMe	O	4	**4l**	92	-
13[e]		OEt	O	4	**4m**	95	-
14[e]		OMe	O	6	**4n**	82	-
15[e]		OMe	O	4.5	**4o**	78	-
16		OEt	S	2	**4p**	94	6g
17		OEt	S	2.5	**4q**	88	1a
18		OMe	S	2	**4r**	90	6g
19		OMe	S	2	**4s**	92	1a
20		Me	O	4.5	**4t**	95	1a
21		Me	O	5	**4u**	91	8d
22		Me	O	4.5	**4v**	94	5g

[a]Reaction conditions: Aldehyde (1 mmol), β-dicarbonyl compound (1 mmol), urea/thiourea (1.5 mmol), EtOH (10 mL), $B(C_6F_5)_3$ (1 mol%), reflux. [b]R_2 = OEt **2a**, R_2 = OMe **2b**, R_2 = Me **2c**. [c]X = O **3a**; X = S **3b**. [d]Isolated yield. [e]Novel compound.



Scheme 2. $B(C_6F_5)_3$ catalyzed 5 g scale synthesis of monastrol.



Scheme 3. Plausible mechanism for dihydropyrimidinones synthesis using $B(C_6F_5)_3$.

intramolecular cyclo-addition and concomitant loss of water to afford dihydropyrimidinone (**4a**) (scheme 3).

4. Conclusions

We have demonstrated an extremely facile and efficient protocol for the synthesis of 3,4-dihydropyrimidin-2-(1*H*) ones and their thione analogues *via* one-pot cyclocondensation of aldehydes, urea/thiourea and β-ketoester/β-diketone using catalytic amount of $B(C_6F_5)_3$. The resulting protocol was proved to be suitable for a wide range of substrates. Furthermore, the present methodology was effectively extended to the large-scale synthesis of monastrol, which signifies its suitability for industrial application. Moreover, this method offers several advantages including mild reaction conditions, eco-friendliness, low catalyst loading, low toxicity, short reaction time, high yields and purity. Another important aspect of this procedure is tolerance of acid-sensitive protecting groups such as TBDMS and TBDPS and compatibility with a variety of functional groups under the present reaction conditions.

Supplementary Information

Spectral data for the synthesized compounds can be accessed at www.ias.ac.in/chemsci.

Acknowledgements

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