



## Brønsted Acidic 1-Ethyl-1,2,4-Triazolium Phenylsulfonate as Catalyst for Biginelli Reaction

G. PUTHUKKUDY<sup>1</sup>, S. NAGARAJAN<sup>2</sup> and E. KANDASAMY<sup>1,\*</sup>

<sup>1</sup>Department of Sciences, Amrita School of Engineering Coimbatore, Amrita Vishwa Vidyapeetham, Amritanagar, Coimbatore-641 112, India

<sup>2</sup>Department of Science and Humanities, PSN Engineering College, Melathediyoore-627 152, India

\*Corresponding author: Fax: +91 422 2656274; Tel: +91 422 265564; E-mail: [k\\_elango@cb.amrita.edu](mailto:k_elango@cb.amrita.edu); [elangoomc@gmail.com](mailto:elangoomc@gmail.com)

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A Brønsted acidic 1-ethyl-1,2,4-triazolium phenylsulfonate has been synthesized and characterized. A catalytic study is performed for 1-ethyl-1,2,4-triazolium phenylsulfonate as acid catalyst for a multicomponent reaction of synthesis of series of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones and their derivatives have been employed and the results were discussed in detail.

**Keywords:** Biginelli reaction, Dihydropyrimidones/thiones, Triazolium salts, Ionic liquids, Pyrimidones.

### INTRODUCTION

Multicomponent reactions (MCRs) are one-pot synthesis methodology has given new pathway to form three or more carbon-carbon bond formation [1]. The Biginelli reaction is one of the examples of multicomponent reactions [2,3]. Mainly, dihydropyrimidinones/thiones (DHPMs) have employed as calcium channel blockers, antiviral, antimitotic, anticarcinogenic and antihypertensive agents [4]. The derivatives of dihydropyrimidinones/thiones are essential substructure in many biologically active natural products [5].

Numerous examples of catalysts were used to improve the quality and quantity of DHPMs in the past one century. The DHPMs synthesis in environmental benign route is an outstanding area of research. The green chemistry is suitable for the above mentioned route and many green catalysts were used to synthesize DHPMs and the ionic liquids is one of them [6-10]. In Biginelli reaction, chemists used number of catalyst like metal salts such as LiBr, FeCl<sub>3</sub>/Si(OEt)<sub>4</sub>, Cu(OTf)<sub>2</sub>, CeCl<sub>3</sub> [11-18]. Many types of zeolite catalyzed and inorganic acid catalyzed have been reported for the synthesis of dihydropyrimidinones/thiones [19-21]. However, the above catalyst used in Biginelli reaction protocols are coupled with certain limitations such as less biodegradability of the catalyst, costly reagents for the synthesis of catalyst, drastic reaction conditions and generation of chemical wastages. In the case of metal catalysts are resulted in excess of oxidized product and substantial amount of metal ion waste

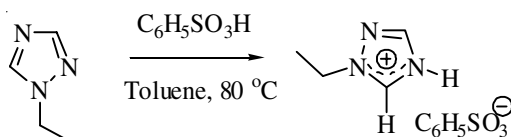
to the environment. These are added major problems to a sustainable process. The synthesis of organic, inorganic and any materials employed by green technology is a leading and challenging task in any field of research. In this perspective, several new chemical compounds have been developed as a catalyst. One among them is ionic liquids. Particularly, ionic liquids such as cmmim[BF<sub>4</sub>], [Gly]NO<sub>3</sub>, bmim[MeSO<sub>4</sub>], Hmim[HSO<sub>4</sub>], bmim[OH] and 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGT) have been known to achieve this transformation [22-26]. The interest to synthesis a new example of triazolium based salt and improvement of reusable and eco-friendly catalytic transformations. In this article, Brønsted acidic 1-ethyl-1,2,4-triazolium phenylsulfonate (TrHEtPS) has been used as a catalyst for one pot synthesis of dihydropyrimidinones/thiones by Biginelli reaction.

### EXPERIMENTAL

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 and 300 MHz, respectively. Elemental analyses of synthesized compounds were obtained from thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Waters Q-TOF Premier mass spectrometer. LC-MS analyses were done on an Agilent MSD mass spectrometer. Method info A: HCOOH in H<sub>2</sub>O, B: 0.04 % HCOOH in CH<sub>3</sub>CN; flow rate: 2.0 mL/min; Column: Chromolith RP-18e, 100-3 mm,

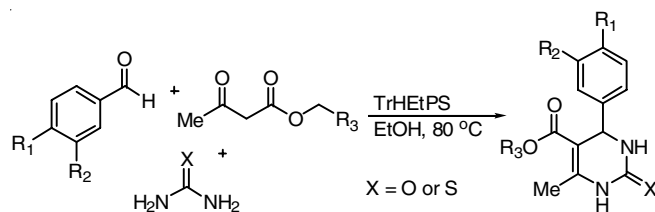
positive mode. The corrected melting points were measured in DALAL melting point apparatus, India. Freshly distilled solvents were used and glassware were dried in oven at 100 °C for overnight. 1,2,4-Triazole and ethyl bromide phenyl sulfonic acid was purchased from sigma Aldrich. All the chemicals were used without further purification.

**Synthesis of 1-ethyl-1,2,4-triazolium phenylsulfonate (TrHEtPS):** Phenyl sulfonic acid (10 mmol) was added dropwise in toluene (10 mL) solution of 1-ethyl-1,2,4-triazoles (10 mmol). This reaction mixture was kept at 80 °C and stirred for 12 h (Scheme-I). Then the reaction mixture was cooled to room temperature and excess of toluene was removed by decanting and the resulting mixture was washed with hexane (15 mL) and dried over vacuum to afford desired product.



**Scheme-I:** Synthesis of 1-alkyl-1,2,4-triazolium based Brønsted acidic ionic liquids

**General Procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones:** Catalyst 1-ethyl-1,2,4-triazolium phenylsulfonate (TrHEtPS) (10 mol) was added to a solution of urea or thiourea (2.0 mmol),  $\beta$ -ketoester (1.5 mmol) and aldehyde (1.0 mmol) in ethanol (0.5 mL). The reaction mixture was heated at 70 to 80 °C for the specified time (0-5 h) (Scheme-II). The completion of the reaction was monitored by thin layer chromatography (ethyl acetate:hexane::4:1) and then the reaction mixture was cooled to room temperature. Then, quenched with mixture of water: ethanol (5:0.5 mL). The obtained solid product was filtered, and washed with *n*-hexane (5 mL) and afforded 3,4-dihydropyrimidin-2(1H)-ones or 3,4-dihydropyrimidin-2(1H)-thiones.



**Scheme-II:** Synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones in TrHEtPS

**Spectral data for Brønsted acidic 1-ethyl-1,2,4-triazolium phenylsulfonate:** Colourless solid, (2.31 g, yield 90 %), Anal. Calcd. (%) for  $C_{11}H_{15}N_3O_3S$  (269.08); C, 49.06; H, 5.61; N, 15.60, Found: C, 49.01; H, 5.54; N, 15.51.  $^1H$  NMR (DMSO- $d_6$  400 MHz): 9.77 (s, 1H, 5-CH), 8.90 (s, 1H, 3-CH), 8.57 (s, 1H, NH) 7.66 (dd, 2H, arom. CH), 7.35 (m, 3H, arom. CH) 4.33 (t, 2H, N-CH<sub>2</sub>-), 1.4 (t, 3H, CH<sub>3</sub>).  $^{13}C$  NMR (DMSO- $d_6$  100 MHz): 147.50 (C-quaternary), 145.03 (C-5), 141.66 (C-3), 129.20, 128.57, 125.69 (C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>), 46.30 (N-CH<sub>2</sub>), 14.25 (-CH<sub>3</sub>). ES-MS  $m/z$ : 98.13 [M- C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>]<sup>+</sup>.

**Spectral data of 3,4-dihydropyrimidin-2(1H)-ones/thiones**

**Methyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table-3, entry 1):** Colourless solid,

95 % yield.  $^1H$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.3 (s, 1H), 7.3 (m, 5H), 5.9 (s, 1H), 5.3 (d,  $J$  = 4.0 Hz, 1H), 3.6 (s, 3H), 2.3 (s, 3H);  $^{13}C$  NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  166.1, 153.5, 146.6, 143.6, 128.7, 127.9, 126.5, 101.1, 55.5, 51.1, 18.7.

**Methyl-4-(4-isopropylphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate: (Table-3.15, entry 3):** Colourless solid, 88 %.  $^1H$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.4 (s, 1H), 7.2 (m, 4H), 5.8 (s, 1H), 5.3 (d,  $J$  = 4.0 Hz, 1H), 3.6 (s, 3H), 2.9 (m, 1H), 2.3 (s, 3H), 1.2 (d,  $J$  = 8.0 Hz, 6H);  $^{13}C$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  166.2, 153.7, 148.5, 146.5, 141.0, 126.8, 126.4, 101.3, 55.2, 51.16, 33.7, 23.9, 18.6.

**Ethyl-4-(3-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate: (Table-3, entry 16):** Pale brown solid, 74 %.  $^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.3 (s, 1H), 9.1 (d,  $J$  = 1.6 Hz, 1H), 7.6 (m, 1H) 7.0 (t,  $J$  = 8.0 Hz, 1H), 6.6 (m, 2H), 6.6 (m, 1H), 5.0 (s, 1H), 3.9 (q, 2H), 2.4 (m, 3H), 1.0 (t,  $J$  = 7.2 Hz, 3H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  165.4, 157.3, 152.2, 148.1, 146.2, 129.3, 116.9, 114.19, 113.1, 99.4, 59.2, 53.8, 17.7, 14.1.

**Ethyl-4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table-3, entry 32):** Pale brown solid, 72 %.  $^1H$  NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  10.2 (s, 1H), 9.5 (d, 1H), 9.4 (s, 1H), 7.1 (m, 1H), 6.6 (d, 3H), 5.0 (d, 1H), 4.0 (q, 2H), 2.2 (s, 3H), 1.1 (t,  $J$  = 7.2 Hz);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  174.1, 165.1, 157.4, 144.8, 144.7, 129.4, 117.0, 114.6, 113.2, 100.7, 59.5, 53.9, 17.1, 14.0.

## RESULTS AND DISCUSSION

The catalyst *i.e.*, 1-ethyl-1,2,4-triazolium phenylsulfonate (TrHEtPS) was synthesized and characterized by ESI-MS,  $^1H$  NMR,  $^{13}C$  NMR and CHN analysis. In  $^1H$  NMR, 5-CH and 3-CH protons were resonated at  $\delta$  10.2 and 8.5 ppm, respectively. In addition, the positive ion ESI-MS<sup>+</sup> gave the corresponding cationic ([M-X]<sup>+</sup>) peak at 98.13  $m/z$ . The pH of TrHEtPS was 3.58 (5 mmol of TrHEtPS was dissolved in 10 mL of trippled distilled water). It was well noted that without TrHEtPS, the reaction did not yield any product (Table-2, entry 1). Initially, TrHEtPS was tested as a catalyst and solvent for acid catalyzed Biginelli reaction and urea, ethyl acetoacetate and benzaldehyde as reagents. It was found that in the absence of solvent dihydropyrimidinone obtained in 80-85 % yield, which indicates that TrHEtPS may be used as a solvent and catalyst (Table-1, entry 1).

In order to find the suitable solvents for the synthesis of dihydropyrimidinones/thiones in different solvent systems were

TABLE-1  
SOLVENTS STUDIES FOR BIGINELLI REACTION IN TrHEtPS

S. No	Solvent	Time (hh:mm)	Yield (%) <sup>b</sup>
1	Neat	1:0	81
2	Water	1:0	54
3	Methanol	1:0	60
4	Ethanol	0:45	93
5	Dichloromethane	1:0	45
6	Toluene	1:0	0
7	Tetrahydrofuran	1:0	34
8	Acetonitrile	1:0	55

<sup>a</sup>Reaction conditions: benzaldehyde (1.0 mmol), ethyl acetoacetate (1.5 mmol), urea (2.0 mmol) and TrHEtPS (10 mol %); <sup>b</sup>isolated yield.

used and their results are accessible in Table-2. The ethanol was found to be most suitable solvent for this reaction. However, other protic solvents like water and methanol resulted with moderate yield and non-polar solvents such as toluene no reaction. Also polar aprotic solvents like THF, CH<sub>3</sub>CN and dichloromethane yielded low.

TABLE-2  
OPTIMIZATION OF REACTION CONDITIONS FOR  
BIGINELLI REACTION USING TrHEtPS

S. No	mmol (%)	Time (hh:mm)	Yield (%)
1	0	1:0	0
2	5	1:0	70
3	10	1:00	87
4	15	0:45	81
5	20	0:25	77

Another set of reactions were done to check whether the yield of reaction is increasing when the amount of catalyst was being increased. The product yield increased from 70 to 87 % when the catalytic amount increased to 10 mol %, from 5 mol %. However, the conversion time did not change it remains an hour. Further increasing the amount of TrHEtPS, the yield of DHPMs was decreased. This might be excess loading of catalyst and acidic nature of TrHEtPS leads in the formation of undesired compounds. After extensive screening of standard reaction,

the following reaction conditions were optimized to compare the catalytic activity of the catalyst, TrHEtPS (10 mol %), urea or thiourea (2.0 mmol),  $\beta$ -ketoesters (1.5 mmol) and aldehyde (1.0 mmol) in ethanol as solvent at 70 to 80 °C to provide DHPMs. Different examples of reactants were tested having later optimized conditions to synthesize dihydropyrimidinones/thiones (DHPMs). The Biginelli reaction products obtained by varying different substituent in aldehyde and the results are presented in Table-3.

The reaction of 4-methyl benzaldehyde with ethyl/methyl acetoacetate carried out to get methyl substituted 3,4-dihydropyrimidin-2-ones and 3,4-dihydropyrimidin-2-thiones in good isolated yields. The yield slightly increased when 4-isopropyl benzaldehyde and 4-methoxy benzaldehyde was used. Out of three halides, substituted benzaldehyde favours 4-chlorobenzaldehyde than 4-bromobenzaldehyde and 4-fluorobenzaldehyde. The 3-hydroxy benzaldehyde resulted less yield when compared to all benzaldehydes. Probably, alkyl substituents in ionic liquids have significant steric effects, which impact the rate of Biginelli reaction. Moreover, 1-ethyl-1,2,4-triazolium phenylsulfonate salt shows better results in the synthesis of dihydropyrimidinones/thiones derivatives.

The reusability of TrHEtPS for reaction of ethylacetoacetate, benzaldehyde and urea, were tried and the results are given in Table-4. The catalyst was recovered from the reaction mixture

TABLE-3  
SYNTHESIS OF 3,4-DIHYDROPYRIMIDIN-2(1*H*)-ONES AND THIONES IN TrHEtPS USING BIGINELLI REACTION

Entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	X	Time (hh:mm)	Yield <sup>b</sup> (%)	mp (°C)
1	H	H	H	O	01:00	92	208-209
2	4-CH <sub>3</sub>	H	H	O	01:30	84	211-212
3	4- <sup>i</sup> Pr	H	H	O	02:30	84	178-179
4	4-OCH <sub>3</sub>	H	H	O	02:15	86	190-191
5	4-F	H	H	O	04:30	73	191-192
6	4-Cl	H	H	O	03:45	82	204-205
7	4-Br	H	H	O	04:00	75	218-219
8	H	3-OH	H	O	01:30	72	221-222
9	H	H	CH <sub>3</sub>	O	01:00	87	201-202
10	4-CH <sub>3</sub>	H	CH <sub>3</sub>	O	02:00	81	212-214
11	4- <sup>i</sup> Pr	H	CH <sub>3</sub>	O	02:00	88	140-141
12	4-OCH <sub>3</sub>	H	CH <sub>3</sub>	O	03:00	85	200-201
13	4-F	H	CH <sub>3</sub>	O	04:30	71	173-174
14	4-Cl	H	CH <sub>3</sub>	O	04:00	81	215-216
15	4-Br	H	CH <sub>3</sub>	O	04:00	74	214-215
16	H	3-OH	CH <sub>3</sub>	O	04:00	65	164-165
17	H	H	H	S	02:00	90	220-222
18	4-CH <sub>3</sub>	H	H	S	02:30	83	154-155
19	4- <sup>i</sup> Pr	H	H	S	04:30	84	169-171
20	4-OCH <sub>3</sub>	H	H	S	03:30	91	177-178
21	4-F	H	H	S	04:30	77	183-184
22	4-Cl	H	H	S	02:30	76	152-153
23	4-Br	H	H	S	04:00	75	178-179
24	H	3-OH	H	S	01:45	69	207-209
25	H	H	CH <sub>3</sub>	S	02:30	81	204-209
26	4-CH <sub>3</sub>	H	CH <sub>3</sub>	S	03:00	82	191-193
27	4- <sup>i</sup> Pr	H	CH <sub>3</sub>	S	04:30	89	138-140
28	4-OCH <sub>3</sub>	H	CH <sub>3</sub>	S	03:00	86	154-155
29	4-F	H	CH <sub>3</sub>	S	04:00	69	186-187
30	4-Cl	H	CH <sub>3</sub>	S	03:30	72	192-193
31	4-Br	H	CH <sub>3</sub>	S	04:00	70	190-191
32	H	3-OH	CH <sub>3</sub>	S	02:30	64	182-183

<sup>a</sup>Reaction conditions: benzaldehyde (1.0 mmol), ethyl acetoacetate (1.5 mmol), urea (2.0 mmol) and TrHEtPS (10 mole %); <sup>b</sup>Isolated yield;

<sup>c</sup>Corrected melting points were verified with reference no. [Ref. 27]

TABLE-4  
CATALYST REUSABILITY STUDY OF TrHEtPS

Entry	Cycle	Time (hh:mm)	Yield (%)
1	0	1:00	87
2	1	1:15	85
3	2	1:15	84
4	3	1:15	82

by using vacuum filtration technique. The crude mixture was then washed with mixture of ethyl acetate and hexane (1:4), and finally dried over vacuum for 1 h.

## Conclusion

In this study, a convenient and reusable procedure for the synthesis of dihydropyrimidinones/thiones using 1,2,4-triazolium phenylsulfonate salt as a catalyst have been reported. The products 3,4-dihydropyrimidin-2(1*H*)-thiones and 3,4-dihydropyrimidin-2(1*H*)-ones has been isolated in range of moderate to good yield. The products were separated from reaction mixture by simple filtration technique, thus the procedure is free from chromatographic purification. It may be pointed out that the recovered catalysts were reused to study their catalytic activity and the loss of its catalytic activity was 2 % for each cycle.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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