

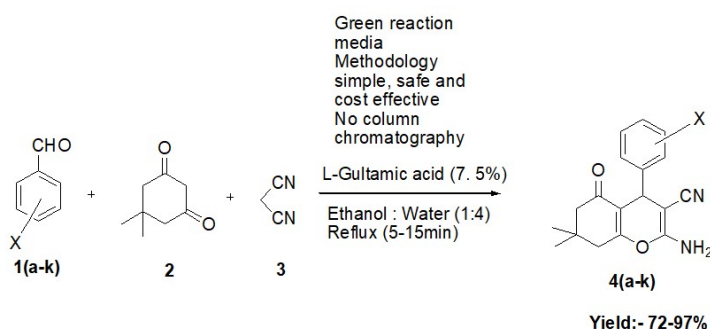
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# Green and Efficient One-pot Synthesis of Tetrahydrobenzo[b]pyran Derivatives

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Glutamic acid is used as an efficient organocatalyst for one-pot synthesis of tetrahydrobenzo [b]pyran via condensation of an aromatic aldehyde, dimedone and malononitrile in ethanol: water (1:4) as solvent at reflux temperature. The short reaction time, cleaner reaction, and easy workup make this protocol practical and economically attractive.

## Graphical abstract



## Keywords

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## 1. Introduction

Multi-component reactions, by virtue of their convergence are widely applied in pharmaceutical chemistry in order to producing different structures, combinatorial libraries for drug discover [1], and environmentally benign perception has received ample attention due to the prospect of compliance with green chemistry principles [2,3]. The major advantages of multicomponent reactions are high atom-economy, operational simplicity, high selectivity, due to substantial minimization of waste, time, labor and cost [4]. 4*H*-pyrans belong to an important class of heterocyclic compounds having important pharmacological and biological activities [5]. They have use in spasmolytic [6], diuretic [7], antiallergic, antibacterial [8], anticoagulant, anticancer and anti-anaphylactic activities [9].

In recent years, Various methods have been reported for the synthesis of 4*H*-pyran and its derivatives via three-component condensations including the use of various media or catalysts such as hexadecyltrimethylammonium bromide (HTMAB) [10], tetra-methyl ammonium hydroxide [11], sodium selenate (Na<sub>2</sub>SeO<sub>4</sub>) [12], PEG1000-DAIL [13], amberlite IRA400 (OH-) [14], tetrabutylammonium bromide (TBAB) [15], trisodium citrate [16], phenylboronic acid (Ph B(OH)<sub>2</sub>) [17], Potassium phthalimide-N-oxyl (POPINO) [18], starch solution [19], tetrabutylammonium fluoride (TBAF) [20], NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub> 12H<sub>2</sub>O (Alum) [21], Nano-kaolin-TiCl<sub>4</sub> [22], CuFe<sub>2</sub>O<sub>4</sub>.starch [23], Dendrimeric magnetic nanoparticle [24] and ceria-vanadia/silica [25]. Some of the previous methods have posed a number of problems such as lengthy procedures, being

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highly corrosive, using expensive catalysts, volatile solvent, laborious work-up and high energy consumption caused by the high temperature reaction. Furthermore, there has been an intense demand for developing a new and green protocol for synthesizing 4H-pyran derivatives.

## 2. Material and Methods

### Materials

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. All yields refer to isolated products unless otherwise stated. Melting points were determined in an open capillary.  $^1\text{H}$  nuclear magnetic resonance (NMR) (400 MHz) with tetramethylsilane as internal standard and dimethylsulfoxide- $d_6$  as solvent. Fourier transform infrared (IR) spectra were obtained as KBr discs on a Shimadzu spectrometer. Mass spectra (MS) were obtained on a Varian-Saturn 2000 GC/MS instrument

### General Procedure for the synthesis of tetrahydrobenzo[b]pyran (4a-K)

A mixture of aromatic aldehyde (1mmol), dimedone (1mmol) and malononitrile (1mmol) in the presence of L-Glutamic acid. (7.5mol %) as catalyst in 5ml ethanol: water (1:4) as solvent was stirred at reflux temperature. After completion of reaction, the mixture was cooled down than poured onto 15 to 20ml of ice-cold water, then the solid product obtained was filtered. The crude solid material was purified by recrystallization from ethanol.

### Spectroscopic data of the synthesized compounds

**2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-chromene-3-carbonitrile (4a):** IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3339, 3269, 3180, 2944, 2190, 1682, 1657, 1211, 1029.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.92 (s, 3H), 1.04 (s, 3H), 2.04-2.15 (m, 2H,  $\text{CH}_2$ ), 2.18-2.29 (m, 2H,  $\text{CH}_2$ ), 4.10 (s, 1H), 5.80 (br s, 2H  $\text{NH}_2$ ), 7.21-7.91 (m, 5H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 28.12, 29.30, 32.17, 35.77, 47.41, 56.99, 111.04, 118.99, 125.01, 130.31, 147.4, 153.35, 159.42, 164.51, 166.76, 196.43.

**2-amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4b):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3370, 3321, 3128, 2932, 2232, 1716, 1656.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.93 (s, 3H,  $\text{CH}_3$ ), 1.05 (s, 3H,  $\text{CH}_3$ ), 2.05-2.11 (m, 2H,  $\text{CH}_2$ ), 2.13-2.24 (m, 2H,  $\text{CH}_2$ ), 4.11 (s, 1H, CH), 5.89 (br s, 2H,  $\text{NH}_2$ ), 7.49 (m, 3H, Ar), 8.21 (d, 1H, Ar  $J$  = 8.1Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.15, 28.42, 32.11, 36.91, 52.43, 58.23, 116.11, 121.90, 126.31, 131.32, 147.77, 154.82, 158.11, 159.14, 159.44, 164.52, 194.

**2-amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4c):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3369, 3322, 3131, 2945, 2222, 1716, 1656.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.94 (s, 3H,  $\text{CH}_3$ ), 1.05 (s, 3H,  $\text{CH}_3$ ), 2.04-2.10 (m, 2H,  $\text{CH}_2$ ), 2.11-2.22 (m, 2H,  $\text{CH}_2$ ), 4.12 (s, 1H, CH), 5.87 (br s, 2H,  $\text{NH}_2$ ), 7.44 (d, 2H, Ar,  $J$  = 8.1 Hz), 8.20 (d, 2H, Ar,  $J$  = 8.1 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.23, 28.67, 32.13, 36.90, 52.14, 58.13, 116.19, 121.98, 126.36, 131.30, 147.75, 154.83, 158.15, 164.55, 194.89.

**2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-4H-chromene-3-carbonitrile (4d):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3347, 3319, 3141, 2932, 2227, 1656, 1547, 1352.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.94 (s, 3H,  $\text{CH}_3$ ), 1.04 (s, 3H,  $\text{CH}_3$ ), 2.02-2.12 (m, 2H,  $\text{CH}_2$ ), 2.10-2.24 (m, 2H,  $\text{CH}_2$ ), 4.10 (s, 1H, CH), 5.88 (br s, 2H,  $\text{NH}_2$ ), 7.42 (m, 3H, Ar), 8.26 (d, 1H, Ar,  $J$  = 2.2Hz).  $^{13}\text{C}$  NMR

(100 MHz,  $\text{DMSO}-d_6$ ): 27.20, 28.68, 32.19, 37.95, 54.10, 59.12, 115.13, 120.92, 124.38, 133.32, 148.76, 154.83, 156.71, 157.12, 158.15, 164.53, 198.80.

**2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-4H-chromene-3-carbonitrile (4e):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3372, 3328, 3142, 2960, 2225, 1718, 1663.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.94 (s, 3H,  $\text{CH}_3$ ), 1.04 (s, 3H,  $\text{CH}_3$ ), 2.03-2.11 (m, 2H,  $\text{CH}_2$ ), 2.12-2.23 (m, 2H,  $\text{CH}_2$ ), 4.11 (s, 1H, CH), 5.87 (br s, 2H,  $\text{NH}_2$ ), 7.41 (d, 2H, Ar,  $J$  = 8.1 Hz), 8.14 (d, 2H, Ar,  $J$  = 8.1 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.37, 28.78, 32.07, 35.95, 50.3, 57.99, 112.09, 119.89, 124.30, 129.30, 146.7, 152.81, 159.16, 163.55, 196.

**2-amino-5,6,7,8-tetrahydro-4-(3-hydroxyphenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4f):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3544, 3451, 3422, 2198, 1628.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.94 (s, 3H,  $\text{CH}_3$ ), 0.95 (s, 3H,  $\text{CH}_3$ ), 2.01 - 2.11 (m, 2H,  $\text{CH}_2$ ), 2.12-2.22 (s, 2H,  $\text{CH}_2$ ), 4.14 (s, 1H, CH), 5.87 (s, 2H,  $\text{NH}_2$ ), 6.62-6.60 (d, 1H, Ar-H,  $J$  = 2.1Hz), 6.90 - 6.96 (m, 3H, Ar-H), 9.88 (s, 1H, -OH)  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.44, 27.88, 28.92, 32.10, 34.89, 50.67, 62.38, 112.92, 114.54, 117.70, 121.18, 135.14, 158.18, 158.27, 158.56, 161.99, 162.25, 198.54.

**2-amino-5,6,7,8-tetrahydro-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4g):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3548, 3473, 3416, 2192, 1638.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.97 (s, 3H,  $\text{CH}_3$ ), 0.99 (s, 3H,  $\text{CH}_3$ ), 2.03 - 2.14 (m, 2H,  $\text{CH}_2$ ), 2.16-2.27 (s, 2H,  $\text{CH}_2$ ), 4.11 (s, 1H, CH), 5.87 (s, 2H,  $\text{NH}_2$ ), 6.61-6.59 (d, 2H, Ar-H,  $J$  = 7.5Hz), 6.91-6.89 (d, 2H, Ar-H,  $J$  = 7.5Hz), 9.81 (s, 1H, -OH)  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.47, 27.98, 28.92, 32.10, 34.89, 50.66, 60.38, 113.96, 116.10, 156.14, 128.57, 128.47, 120.08, 158.55, 161.89, 196.14.

**2-amino-5,6,7,8-tetrahydro-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4h):** IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3376, 3319, 3185, 2960, 2190, 1682, 1657, 1606, 1510, 1368, 1256, 1212, 1033.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.93 (s, 3H), 1.06 (s, 3H), 2.06-2.17 (m, 2H,  $\text{CH}_2$ ), 2.19-2.30 (m, 2H,  $\text{CH}_2$ ), 4.12 (s, 1H), 5.86 (br s, 2H  $\text{NH}_2$ ), 3.62 (s, 3H - $\text{OCH}_3$ ), 7.91 (d, 2H,  $J$  = 7.5 Hz), 7.12 (d, 2H,  $J$  = 7.5 Hz) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.32, 28.12, 32.17, 34.85, 51.3, 47.41, 56.99, 111.04, 118.99, 125.01, 130.31, 147.4, 153.35, 159.42, 164.51, 198.

**2-Amino-4-(fur-2-yl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4i):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3470, 3410, 2196, 1638.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.99 (s, 3H,  $\text{CH}_3$ ), 1.02 (s, 3H,  $\text{CH}_3$ ), 2.22 - 2.14 (d, 2H,  $\text{CH}_2$ ), 2.36 - 2.35 (d, 2H,  $\text{CH}_2$ ), 4.46 (s, 1H, CH), 5.24 (s, 2H,  $\text{NH}_2$ ), 6.19 - 6.06 (m, 2H, furyl-H), 7.26 - 7.16 (m, 1H, furyl-H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 26.82, 27.29, 29.93, 29.00, 31.45, 31.91, 32.14, 40.66, 41.28, 50.52, 52.82, 59.12, 105.89, 110.44, 111.33, 119.06, 119.52, 141.57, 154.58, 158.81, 160.56, 162.75, 195.90, 197.64.

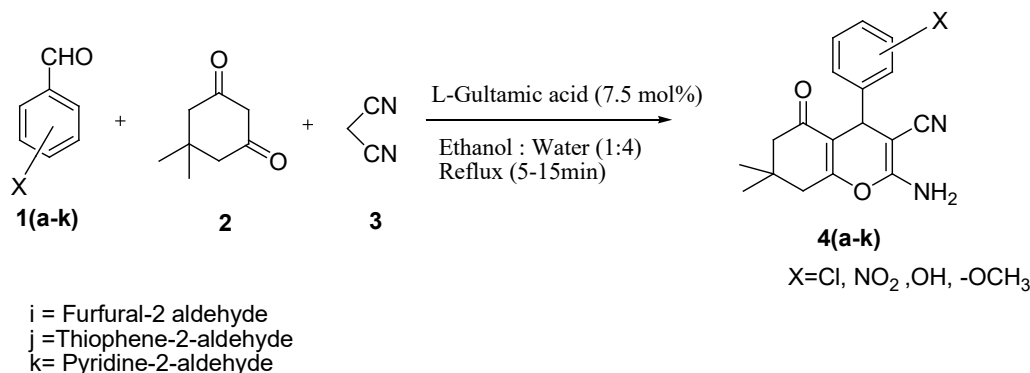
**2-amino-4a,5,6,7,8a-hexahydro-7,7-dimethyl-5-oxo-4-(pyridin-3-yl)-4H-chromene-3-carbonitrile (4k):** IR (KBr) ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3363, 3317, 3131, 2941, 2219, 1712, 1667.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 0.96 (s, 3H,  $\text{CH}_3$ ), 1.05 (s, 3H,  $\text{CH}_3$ ), 2.02-2.13 (m, 2H,  $\text{CH}_2$ ), 2.16-2.27 (m, 2H,  $\text{CH}_2$ ), 4.12 (s, 1H, CH), 5.98 (br s, 2H,  $\text{NH}_2$ ), 7.18-8.17 (m 4H Pyridine-H)  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ): 27.11, 28.41, 32.15, 36.12, 50.3, 112.19, 120.01, 124.30, 129.30, 145.71, 172.81, 169.67, 164.52, 152.23, 196.02.

## 3. Results and Discussion

As a contribution of our research group work devoted to the development of useful synthetic methodologies [ 26-28].

We herein report a facile and efficient methodology for the synthesis of tetrahydrobenzo[b]Pyran. This method involves the efficient synthesis of substituted tetrahydrobenzo[b]Pyran by treatment of 4-hydroxyl benzaldehyde (1mmol),

dimedone (1mmol) and malononitrile (1mmol) and L-Glutamic acid (7.5 mol%) as catalyst dissolved in 5 ml of in ethanol: water (1:4) at reflux temperature for 05- 15 min (Scheme 1).



**Scheme 1.** Facile and green methodology for the synthesis of tetrahydrobenzo[b]Pyran.

To evaluate the effect of solvent, various solvents such as Ethanol, ethanol:water (4:1,v:v), ethanol:water (3:2 v:v), ethanol:water (2:3 v:v) ethanol:water (4:1) and water were used for the model reaction. The desired product was obtained in 67, 74, 74, 70, 96 and 94% yields respectively after respective time at reflux condition. Ethanol:Water: (1:4) stand out as the solvent of choice among the solvents tested. Because of the rapid conversion and excellent yield (96%) of desired product obtained (Table 1, entry 5), whereas the product formed in lower yields (67-94%) in longer time by using other ratio of ethanol and water solvents.

**Table 1.** Screening of solvents.

| Entry | Solvent             | Time      | % Yield |
|-------|---------------------|-----------|---------|
| 1     | Ethanol             | 12:30 hr. | 67%     |
| 2     | Ethanol:water (4:1) | 3:30 hr   | 74%     |
| 3     | Ethanol:water (3:2) | 3:30 hr   | 74%     |
| 4     | Ethanol:water (2:3) | 3:30 hr   | 70%     |
| 5     | Ethanol:water (1:4) | 10 min    | 96%     |
| 6     | Water               | 4:30 hr.  | 94%     |

To determine the appropriate concentration of the catalyst L- Glutamic acid, it has been investigated the model reaction first without catalyst and very less product was obtained (i.e.

trace) at different concentrations of catalyst like 2.5, 5, 7.5 and 10 mol% the product was formed in 57, 76, 96 and 96% yields, respectively (Table 2). This indicates that 7.5 mol% of L- Glutamic acid is sufficient for the best result by considering the reaction time and yield of product.

**Table 2.** Optimization of the amount of L- Glutamic acid.<sup>a</sup>

| Entry | L- Glutamic acid (mol %) | Yield <sup>b</sup> (%) |
|-------|--------------------------|------------------------|
| 1     | 2.5                      | 57                     |
| 2     | 5                        | 76                     |
| 3     | 7.5                      | 96                     |
| 4     | 10                       | 96                     |

<sup>a</sup>Reactions: 1 (1 mmol), 2 (1 mmol), 3 (1mmol) L- Glutamic acid in ethanol:water (4:1) at reflux temperature.; <sup>b</sup>Isolated yields

In order to establish better catalytic activity of L- Glutamic acid, the synthesis of tetrahydrobenzo[b]pyran derivatives was compared with other catalysts reported in literature. As shown in Table 3, synthesis of these compounds catalyzed by L- Glutamic acid in ethanol:water (1:4) offers production of the corresponding products in shorter time, much efficient yield and milder condition, while other methods require more amount of catalyst and longer reaction time for synthesis of tetrahydrobenzo[b]pyrans.

**Table 3.** Effect of different catalysts for the synthesis of tetrahydrobenzo[b]pyran from the condensation of the reaction using an aromatic aldehyde, dimedone and malononitrile.

| Entry | Catalyst.                                                             | Conditions                          | Time          | Yield | Ref.    |
|-------|-----------------------------------------------------------------------|-------------------------------------|---------------|-------|---------|
| 1     | Na <sub>2</sub> SeO <sub>4</sub> 0.1 g                                | EtOH/H <sub>2</sub> O, reflux       | 0.66-3 (h)    | 80-98 | 12      |
| 2     | Trisodium citrate, 5 mol%                                             | EtOH/H <sub>2</sub> O, reflux       | 5-120 (min)   | 80-96 | 16      |
| 3     | PhB(OH) <sub>2</sub>                                                  | H <sub>2</sub> O/EtOH, Reflux       | 10-60 (min)   | 42-95 | 17      |
| 4     | POPINO, 7.5 mol%                                                      | H <sub>2</sub> O, reflux            | 10-40 (min)   | 88-98 | 18      |
| 5     | Starch solution, 4mL                                                  | 50 °C                               | 30-75 (min)   | 82-95 | 19      |
| 6     | TBAF, 10 mol%,                                                        | H <sub>2</sub> O, reflux            | 10-300 (min)  | 73-98 | 20      |
| 7     | NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O | EtOH, 80°C                          | 120-130 (min) | 85-95 | 21      |
| 8     | Nano- kaolin-TiCl <sub>4</sub>                                        | EtOH, Reflux                        | 15 (min)      | 85-94 | 22      |
| 9     | CuFe <sub>2</sub> O <sub>4</sub> @starch                              | EtOH, R.t                           | 20-50 (min)   | 84-96 | 23      |
| 10    | L-Glutamic acid                                                       | EtOH/H <sub>2</sub> O, (1:4) reflux | 5-12 (min)    | 85-97 | Present |

**Table 4.** Synthesis of tetrahydrobenzo[b]pyran using L- Glutamic acid.<sup>a</sup>

| Entry | Product | Aldehyde                                           | Time (min) | Yield <sup>b</sup> (%) | Obt. M.P (°C) | M.P in Literature (°C) |
|-------|---------|----------------------------------------------------|------------|------------------------|---------------|------------------------|
| 1     | 4a      | C <sub>6</sub> H <sub>5</sub> -                    | 11         | 97                     | 229-231       | 231-232 [21]           |
| 2     | 4b      | 2-ClC <sub>6</sub> H <sub>4</sub> -                | 05         | 85                     | 206-208       | 208-210 [7]            |
| 3     | 4c      | 4-ClC <sub>6</sub> H <sub>4</sub> -                | 12         | 96                     | 246-248       | 246 [23]               |
| 4     | 4d      | 3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -  | 08         | 96                     | 211-212       | 212-213 [21]           |
| 5     | 4e      | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -  | 05         | 93                     | 179-181       | 180-182 [23]           |
| 6     | 4f      | 3-OHC <sub>6</sub> H <sub>4</sub> -                | 07         | 97                     | 225-226       | 226-228 [24]           |
| 7     | 4g      | 4-OHC <sub>6</sub> H <sub>4</sub> -                | 15         | 96                     | 209-210       | 207-209 [21]           |
| 8     | 4h      | 4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> - | 09         | 72                     | 192-193       | 190-192 [21]           |
| 9     | 4i      | C <sub>4</sub> H <sub>3</sub> O-                   | 08         | 98                     | 226-228       | 228-230 [17]           |
| 10    | 4j      | C <sub>4</sub> H <sub>3</sub> S-                   | 07         | 88                     | 215-217       | 216-218 [25]           |
| 11    | 4k      | C <sub>5</sub> H <sub>4</sub> N-                   | 15         | 90                     | 190           | -----                  |

<sup>a</sup>Reactions: 1 (1 mmol), 2 (1 mmol), 3 (1mmol) and L- Glutamic acid (7.5 %) as catalyst in ethanol:water (4:1) at reflux temperature.;<sup>b</sup>Isolated yields

To study the generality of this process, a variety of examples were illustrated for the synthesis of tetrahydrobenzo[b]pyran and the results are summarized in Table 4. The reaction is compatible for various substituents such as -CH<sub>3</sub>, -OCH<sub>3</sub>, -OH, and -Cl. The formation of desired product has been confirmed by <sup>1</sup>H NMR and IR spectroscopic analysis techniques and compared with the corresponding literature data.

## 4. Conclusions

In conclusion, this method has described a simple and proficient approach for the synthesis of tetrahydrobenzo[b]pyran using L- Glutamic acid as catalyst and aqueous alcoholic as solvent. Present methodology offers very attractive features such as simple experimental procedure, higher yields and economic viability, when compared with other method as well as with other catalysts, and will have wide scope in organic synthesis.

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## Author Contributions

Bhaskar P. Ankush: Performed the experiments, Contributed reagents, materials, analysis tools or data. Balasaheb V. Shitole: carried out data analysis, interpreted the results. Nana V. Shitole: methodology, review, investigation, drafted manuscript and supervision.

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